

Lignin Phenol Formaldehyde Wood Adhesives

Master Thesis

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Zusammenfassung

Aufgrund seiner phenolischen Struktur und der großen vorhandenen Menge von Lignin gibt es das Bestreben, Lignin als Ersatz für Phenol in phenolischen Klebstoffen einzusetzen. Ziel der Masterarbeit war es, ein Herstellungsverfahren für Lignin-Phenol-Formaldehyd Harze zu entwickeln. Der Phenolanteil der Harze wurde dabei mit bis zu 40% Lignin ersetzt. Die Hypothese war, dass Lignin-Phenol-Formaldehyd-Klebstoffe mit gleichen Eigenschaften wie gewöhnliche Phenol-Formaldehyd-Klebstoffe hergestellt werden können. Dazu wurden Harze mit 5, 10, 20, 30 und 40% Lignin, bezogen auf die Masse von Phenol, hergestellt, sowie ein Referenzklebstoff mit 0% Lignin. Für die Tests wurden Sarkanda Gras Soda Lignin und Kiefer Kraft Lignin Indulin AT™ eingesetzt. Zu Beginn wurden Screeningtests zur Bestimmung einer geeigneten Synthesetemperatur durchgeführt. Im Anschluss daran wurde geprüft, ob das Verfahren reproduzierbar ist. Während dieser Versuche wurden der Ablauf und die verwendeten Apparaturen mehrmals geändert, um die Harzsynthese zu optimieren. Unter Nutzung des optimierten Ablaufes wurden Harze hergestellt und charakterisiert. Um die Eigenschaften bestimmen zu können, wurden verschiedenen Teststandards verwendet und bei Bedarf angepasst.

Folgende Eigenschaften wurden bestimmt: Viskosität, Festharzgehalt (ISO 3251), B-Zeit (DIN 16916-2) als Maß für die Aushärtezeit, Wasserverdünnbarkeit (ISO 8989) und der Gehalt an freiem Formaldehyd (ISO 11402). Das Aushärteverhalten wurde mit Differential Scanning Calorimetry bestimmt. Ein weiterer wichtiger Punkt war es, die Auswirkung des Ligningehaltes auf die Klebefestigkeit zu bestimmen. Dazu wurden Probekörper für eine Zugscherprüfung in Anlehnung an die ÖNORM EN 302-1 hergestellt, in unterschiedlichen Klimata (Behandlung A1+ und A2) gelagert und geprüft. Die Ergebnisse der Tests haben keine wesentlichen Unterschiede der Eigenschaften gezeigt. Eine Ausnahme stellte der Gehalt an freiem Formaldehyd dar, welcher mit steigender Konzentration von Lignin linear zunahm. Weiters führte ein erhöhter Ligningehalt zu einer verzögerten Aushärtung. Die statistische Analyse der Zugscherprüfung hat gezeigt, dass bei der Behandlung A1+ Probekörper mit reinem Phenol-Formaldehyd und mit 5% Lignin im Mittel eine höhere Festigkeit aufweisen als die Probekörper mit den übrigen Klebstoffen. Bei der Behandlung A2 erreichten die Probekörper mit 20% Lignin eine höhere mittlere Zugscherfestigkeit als die Proben mit 5, 10 und 30% Lignin.

Schlüsselwörter:

B-Zeit, Differential Scanning Calorimetry (DSC), Festharzgehalt, Freies Formaldehyd, Lignin-Phenol-Formaldehyd-Klebstoffe, Viskosität, Wasserverdünnbarkeit, Längszugscherfestigkeit

Abstract

Due to its phenolic structure and the huge available quantities of lignin a lot of efforts to substitute phenol with lignin in phenolic adhesives were already made. The goal of this master thesis was to develop a production procedure for lignin-phenol-formaldehyde resins of which the amount of phenol is replaced up to 40% by lignin. The hypothesis was that it is possible to produce adhesives with equal properties compared to pure phenol-formaldehyde resins. Therefore adhesives with 5, 10, 20, 30 and 40% lignin based on the total mass of phenol were produced as well as a reference resin with 0%. For the tests Sarkanda grass Soda lignin and pine Kraft lignin Indulin AT™ were used. To determine an appropriate synthesis temperature screening tests were performed at the beginning. Subsequently reproducibility tests were conducted. During these tests the procedure and the used equipment were changed to optimize the resin synthesis. The optimized procedure was used to synthesize adhesives which were characterized. To determine the properties different standards were used and if needed adjusted.

The resins were characterized in terms of viscosity, solid content (ISO 3251), B-time (DIN 16916-2) as a value for curing time, water miscibility (ISO 8989) and free formaldehyde content (ISO 11402). The curing development was determined with differential scanning calorimetry. Another important point was to determine the influence of the used amount of lignin on the bonding strength. Therefore specimens for the determination of longitudinal tensile shear strength were manufactured according to the standard ÖNORM EN 302-1, stored in different climates (treatment A1+ and A2) and tested. The results of the tests showed no substantial differences. An exception was the free formaldehyde content which increases linearly with increasing amount of lignin. An increased amount of lignin led to a delayed curing of a resin. The statistical analysis of the tensile shear strength test showed that for treatment A1+ the specimens with pure phenol formaldehyde and 5% lignin show higher mean lap shear strength than the samples with the other adhesives. For treatment A2 the specimens with 20% lignin shows higher values than the groups with 5, 10 and 30% lignin.

Key words:

B-time, differential scanning calorimetry (DSC), free formaldehyde content, lignin-phenol-formaldehyde adhesives, longitudinal tensile shear strength, solid content, viscosity, water miscibility

Index of Abbreviations

A	surface [mm ²]
ABES	automated bonding evaluation system
ANOVA	analysis of variances
DSC	differential scanning calorimetry
FLIPPR	Future Lignin and Pulp Processing Research
LPF x%	lignin-phenol-formaldehyde adhesive with x wt% phenol replacement by lignin (x = 5, 10, 20, 30, 40)
m	mass [g]
MUF	melamin-urea-formaldehyde resin
PF	phenol-formaldehyde resin
PRF	phenol-resorcinol-formaldehyde resin
PUR	polyurethane
PVAc	polyvinyl acetate
s01-s14	resins for screening tests
SC	solid content [%]
t01-t19	resins for reproducibility tests
V	volume [mm ³]
w _{el.}	wood moisture determined with electrical resistance [%]
w _{oven}	wood moisture determined with the oven-dry method [%]

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1. Introduction

Lignin is the second most abundant natural polymer by mass next to cellulose (GOSSELINK et al., 2004; LEWIS et al., 1999) and has beside cellulose a strong impact on the mechanical strength and stiffness of plants. Furthermore it assures water transportation within the xylem with low absorption or evaporated due to its hydrophobic character and finally it increases the resistance against degradation, like opportunistic pathogens, microorganisms and herbivores (LEWIS et al., 1999). Numerically around 70 million tons are accumulated from the pulp and paper industry during wood pulping every year (LORA, 2008).

Lignin can be utilized for many applications such as a binder for animal feed, pellets, bricks, ceramics, and road dust as well as for dispersants in concrete, gypsum, oil drilling products etc. (MCCARTHY and ISLAM, 1999).

The interest to produce wood adhesives from renewable materials has shown up first time in the 1940s. It reached its peak in the early 1970s, during the first oil crisis, but the interest decreased again since the costs of oil declined again as reviewed by PIZZI (2006).

This work was integral part of the subproject Bioadhesives/Lignin based adhesives of the FLIPPR project, which stands for FUTURE LIGNIN AND PULP PROCESSING RESEARCH. It is a cooperative research project between Austrian pulp and paper companies and Austrian universities with the goal to increase the efficiency of the wood compound utilization. This work had the aim to gain knowledge how to make lignin-phenol-formaldehyde adhesives. The developed procedure should be the base for further research.

Main focus was to develop a synthesis procedure for a Lignin-Phenol-Formaldehyde-Resin of defined properties which is reproducible in the first place. Secondly the procedure has to be used to produce resins with 5, 10, 20, 30 and 40% Sarkanda grass Soda lignin as well as a pure phenol-formaldehyde resin in order to see the influence of lignin content. For the latter the pure adhesives have been characterized and adhesive bonds were evaluated by lap shear tests.

1.1 Lignin

Lignins are irregular amphiphilic polymers which are composed of phenyl propane units interlinked by a variety of bond types. The three main phenyl propane units are coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, as shown in Figure 1, which are synthesized by the shikimic acid pathway and afterwards polymerized due to a

enzymatically induced radical reaction to a randomly three dimensional polymer (HENRIKSSON, 2009; ROWELL, 2012; SJÖSTRÖM, 1993).

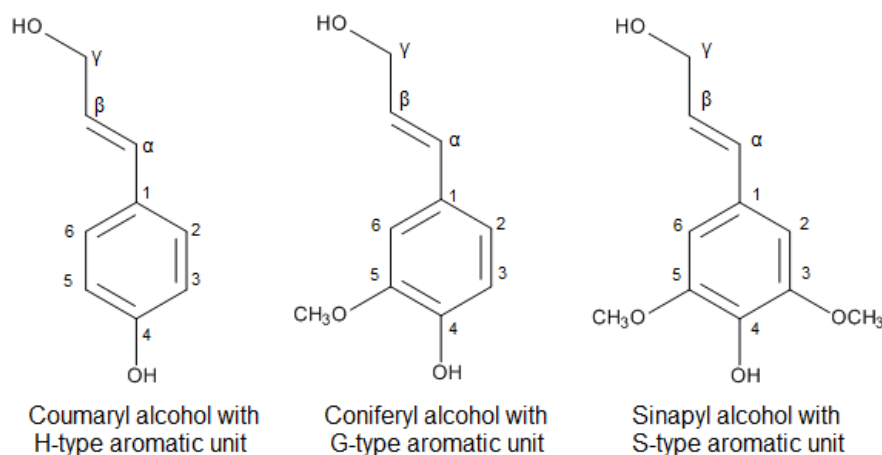


Figure 1: Monomers of lignin
(DE WILD et al., 2012)

During polymerization mainly ether (C-O-C) and carbon to carbon (C-C) bonds are formed, which results in a number of different linkages, whereas the most frequent linkage for softwood and hardwood is the β -O-4 linkage with 35-60% and 40-70% of all linkages. Other main types of linkages are α -O-4, 5-5 (Figure 2), β -5, β - β and 4-O-5 bonds (HENRIKSSON, 2009; ROWELL, 2012; SJÖSTRÖM, 1993).

In lignin these units are named after their aromatic moieties. In Coumaryl alcohol these moiety is called p-hydroxyphenyl (H), in coniferyl alcohol it is called guaiacyl (G) and in sinapyl alcohol it is called syringyl (S). The total amount of lignin is varying among and due to different growth conditions within the wood species. In the temperate climate the lignin content for softwood lies in general between 15% and 35% and for hardwood between 18% and 26% (GULLICHSEN, 2000; HENRIKSSON, 2009; LEWIS et al., 1999; ROWELL, 2012). Hardwood species from the subtropical and tropical area can have higher lignin contents like *Eucalyptus marginata* Sm. of 43% which is common in Australia and *Adenanthera intermedia* Merr. with 35% as an example for the Philippines. The lignin content for softwood in the subtropical and tropical zones do not exceed the content of the temperate climate much (PETTERSEN, 1984).

Depending on the wood species the composition of lignin – the percentage of H-, G- and S-units – differs as well. Guaiacyl (G) is predominating in softwood with small amounts of p-hydroxyphenyl (H) whereas hardwood mainly consists of a combination of guaiacyl (G) and syringyl (S) with small amount of p-hydroxyphenyl (H). Grasses in general show a more equal distribution between p-hydroxyphenyl (H), guaiacyl (G)

and syringyl (S) (Table 1). For all three groups the distribution varies depending on the species (HENRIKSSON, 2009; LEWIS et al., 1999).

Table 1: Distribution of H/G/S units in plants

	H-Unit p-Hydroxyphenyl	G-Unit Guaiacyl	S-Unit Syringyl	Source
Softwoods	5 % <5%	94% >95%	1% None or Trace	(ERICKSON et al., 1973) (HENRIKSSON, 2009)
Hardwoods	0-8%	25-50%	46-75%	(HENRIKSSON, 2009)
Grasses	15-35% 5-33%	50-70% 33-80%	15-35% 20-54%	(FAIX, 2008) (HENRIKSSON, 2009)

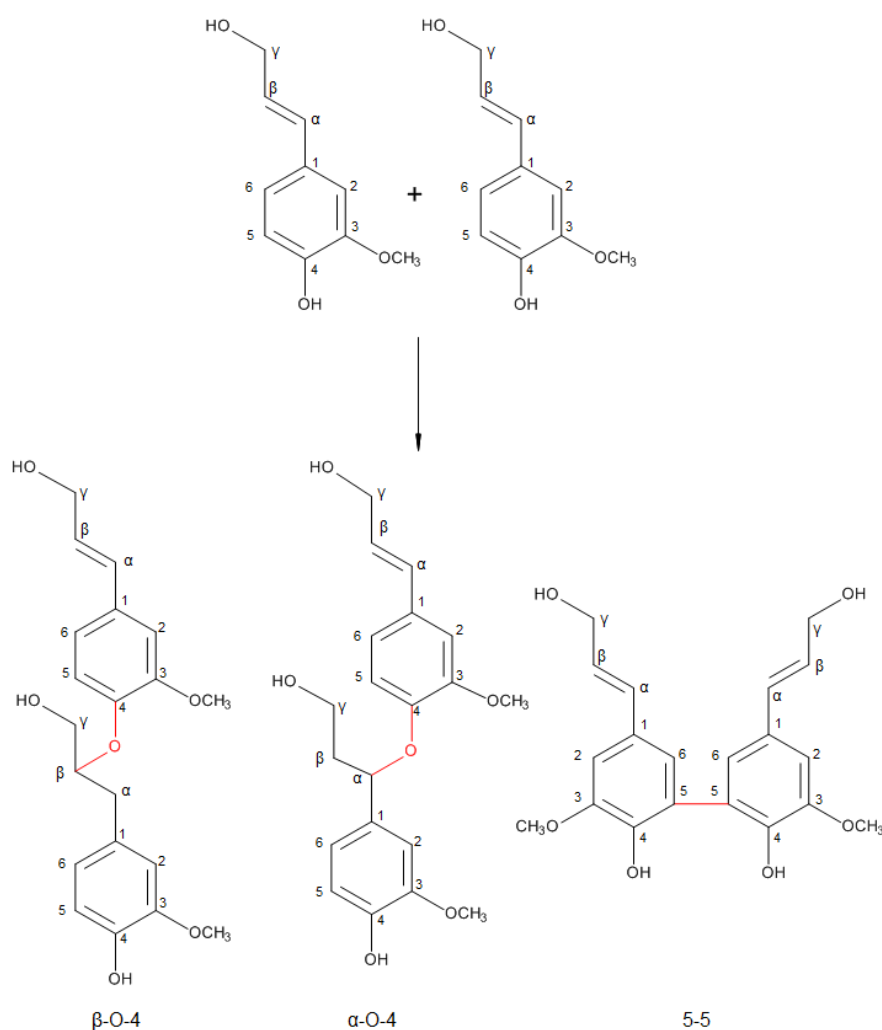


Figure 2: Bond types β-O-4, α-O-4 and 5-5
(SJÖSTRÖM, 1993)

1.2 Wood Pulping

The objective of wood pulping is the cleavage of the interlinkages between lignin, hemicellulose and cellulose and the dissolution of lignin and hemicellulose with the goal to separate the undissolved cellulose fibers. Different pulp procedures are known where delignification is achieved by different chemicals. The three most common chemical pulping procedures in industry are the Soda process, the sulfite process and the Kraft process. Another process which is not yet commercially used but of interest is the Organosolv process.

The Soda process is named after its cooking agent which is caustic soda (sodium hydroxide). The active agents are hydroxyl ions. It was the first chemical pulping process invented in 1851 by Hugh Burges and Charles Watt (SIXTA, 2006). Compared to the Kraft Process it has the advantage that sodium aluminium silicates can be removed. This is an issue for example for bamboo or diverse straw liquors which arise due to higher silica contents (HOLMLUND and PARVIAINEN, 2000). As reviewed in SIXTA (2006) the silica content for bamboo is 1.5% to 3% and respectively 3% to 7% for cereal straw.

Shortly after the soda process the acid sulfite process was invented by Benjamin Tilghman. Sulfur dioxide in combination with different bases such as Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+ are used as chemicals. Sulfonation and hydrolysis are causing delignification in this process. Firstly the hydrophilicity of lignin is increased during the sulfonation with sulfonic acid groups and secondly ether bonds are broken (hydrolysis) (GULLICHSEN, 2000; SIXTA, 2006; SJÖSTRÖM, 1993).

The Kraft process is an enhancement of the soda process and was developed by Carl Dahl and patented by him in 1884. It is operated with white liquor a highly alkaline liquor (pH~14), which consists of sodium hydroxide, sodium sulfide and small amounts of Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, NaCl and CaCO_3 . The main active agents are the OH^- and the HS^- ions which occur from the hydrolyzation of NaOH and Na_2S in water. Due to the higher nucleophilicity of hydrogen sulfide ions compared to hydroxyl ions, the Kraft process shows improved delignification compared to the soda process. Similar as with the sulfite process cleavage of ether bonds are responsible for the depolymerization and the dissolution of lignin in the pulping liquor. This cooking liquor is called black liquor and consists apart from lignin degradation products of carbohydrates and very small amount of extractives (GULLICHSEN, 2000; POTTHAST, 2006; SIXTA et al., 2006; SJÖSTRÖM, 1993).

As reviewed in SUNDQUIST (2000) it has been tried to use organic solvents such as alcohols and organic acids since the 1800s. The first publication of Organosolv pulping dates back to Kleinert and Tayenthal in 1931 who used an alcohol water

mixture to dissolve wood. In this process organic solvents like methanol or ethanol are used.

Besides the above described methods of wood pulping several other methods exist which are listed up in SJÖSTROM (1993) and are not discussed in the thesis. The metal ions remain in the cooking liquor together with the lignin, which can have an effect on the chemical reactions during the resin production. The absence of any metal ions in the Organosolv process may be an advantage for resin synthesis.

1.3 Phenol Formaldehyde Resins

The production of the first phenol formaldehyde condensates dates back to the early 20th century when Dr. Leo Hendrik Baekeland invented highly cross linked phenol-formaldehyde plastics (GARDZIELLA et al., 1999). The general advantages of phenolic resins are high strength levels, long thermal and mechanical stability, low toxicity, excellent electrical and thermal insulation capabilities and excellent cost performance characteristics. Specific advantages which make it of special interest for wood applications are low levels of formaldehyde release, high water resistant, weatherproof characteristics and low thickness swelling of phenolic bonded boards. Disadvantages of this type of resin are the slower hardening compared to aminoplastic resins, dark color of the glue layer, problems with processing of acid wood species or higher moisture absorption of panels which are stored at higher humidity levels due to the hygroscopicity of the used alkali (GARDZIELLA et al., 1999; DUNKY and NIEMZ, 2002). Although some negative points are listed this type of resin is important for the wood industry because of its positive effects. The issue of excellent cost performance is strongly related to the cost of the raw material which is in most cases fossil fuels and can change quite fast.

Main source elements for PF resins are phenol, formaldehyde, sodium hydroxide and water. Phenol and formaldehyde are the main substances which should polymerize to a three dimensional structure. Phenolic resins are divided into resoles and novolacs. The differences are the ratio of formaldehyde to phenol and the pH level at which the reaction takes place. For resoles the ratio is $F/P \geq 1$ under alkaline conditions whereas for novolacs the F/P ratio is <1 which take place under acid conditions. Phenol can be produced from coal, coke oven gases by condensation, waste waters of coal gasification, lignin, low rank coal and from petroleum by various methods. The cumene process is the main industrial process to produce phenol. Almost 95% of the annual production of 8 million tons is synthesized with this process. Cumene is a product of benzene and propene which occurs during alkylation. The preproducts are a consequence of oil cracking. Natural gas is the

main raw material to produce formaldehyde in the methanol process (GARDZIELLA et al., 1999; MOLINARI et al., 2015; VAN LAAK et al., 2010).

The reaction of a phenol with formaldehyde takes place under alkaline conditions and leads in first place to a hydroxymethylation of phenol in ortho and para position which takes place at temperatures below 60°C (Figure 3). The alkaline conditions are adjusted with sodium hydroxide or another base. Formaldehyde exists under basic conditions in aqueous solution as methanediol (HOCH_2OH), which is why water is separated at the step of methylolation (CHRISTIANSEN and GOLLOB, 1985).

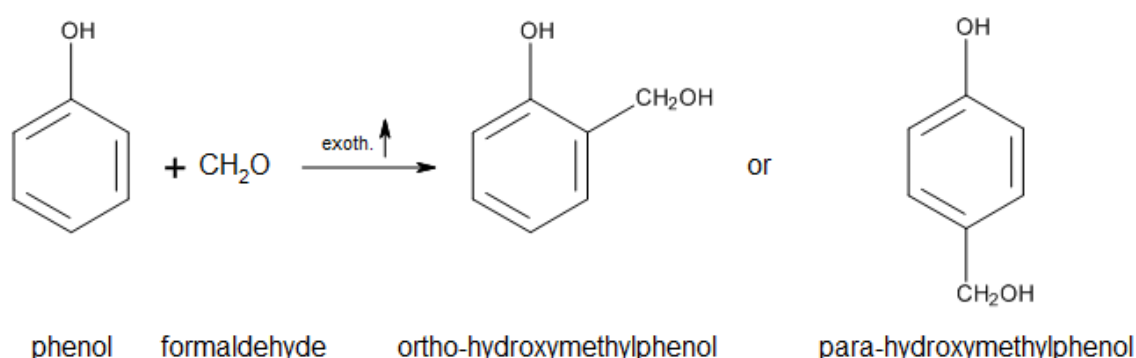


Figure 3: Methylolation of phenol
(CHRISTIANSEN and GOLLOB, 1985)

Figure 3 and Figure 4 show the possible mono, di- and tri methylolated phenolic derivatives.

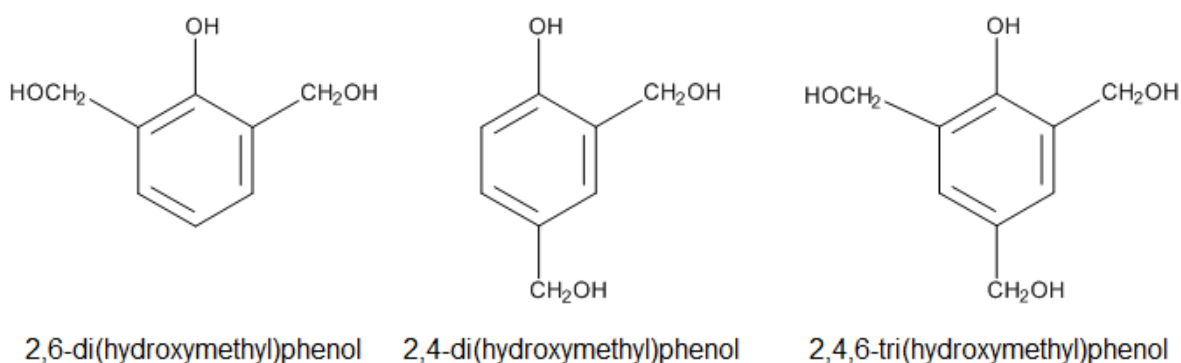


Figure 4: Additional methylated phenol structures
(CHRISTIANSEN and GOLLOB, 1985)

As reviewed in DUNKY and NIEMZ (2002) methylolation is a strong exothermic process, which is why the addition of formaldehyde has to be accomplished slowly. Subsequently poly-condensation takes place which occurs at temperatures above 60°C and leads to oligomers. Depending on the functional groups which are reacting, different dimers can be formed in this second reaction step.

As shown in Figure 5 the (hydroxymethyl)phenoles can react with a second compound which still has an unreacted active ring position of a second molecule

forming a methylene linkage between the two monomers (CHRISTIANSEN and GOLLOB, 1985).

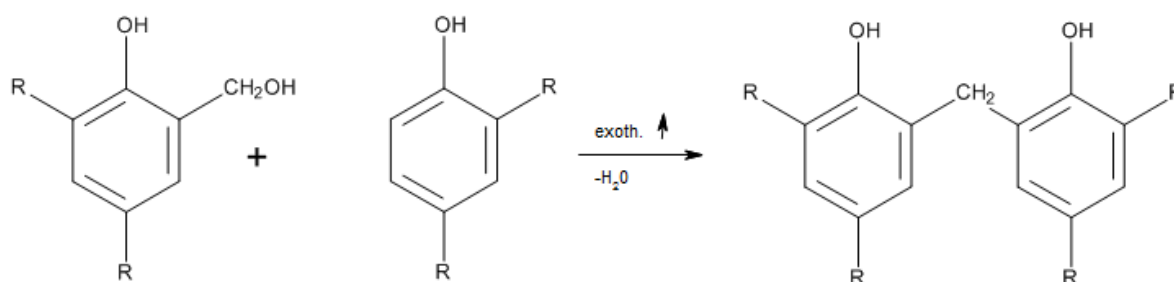


Figure 5: Formation of phenolic dimers linked by methylene bridges
(CHRISTIANSEN and GOLLOB, 1985)

If two hydroxymethyl groups are reacting, an ether bond can be formed whereby water is eliminated (Figure 6).

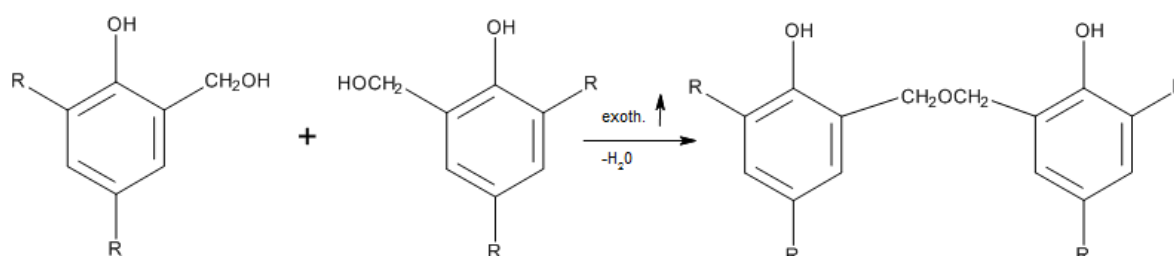


Figure 6: Formation of phenolic dimers linked by ether bonds
(CHRISTIANSEN and GOLLOB, 1985)

Alternatively a mixture of water and formaldehyde is separated where the phenols are connected via a methylene bridge (Figure 7). Ether bonds are usually formed under neutral or acidic conditions and hardly present under alkaline conditions (CHRISTIANSEN and GOLLOB, 1985).

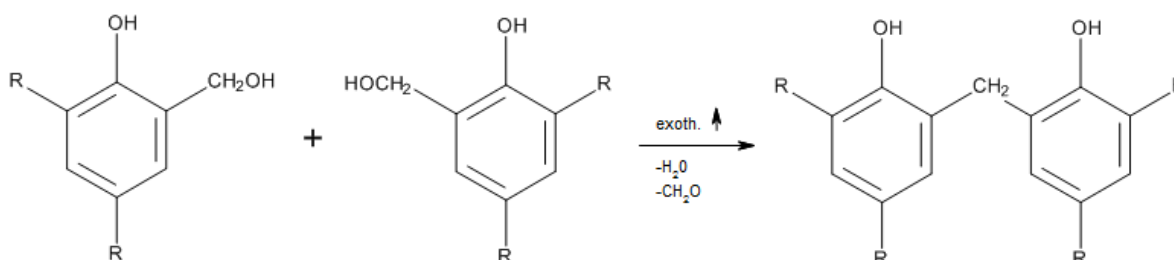


Figure 7: Reaction of equal phenolic moieties leading to a methylene bridge
(CHRISTIANSEN and GOLLOB, 1985)

At equimolar ratio of methylolated phenol and formaldehyde, a competition between addition and condensation occurs (GARDZIELLA et al., 1999). The condensation process finally leads to a three dimensional structure whereby the temperature has to be lowered during final synthesis to reduce the curing rate and to obtain a resin near the target viscosity. PF precondensates consist of oligomeric and polymeric

constituents, that react to three dimensional structures upon the final curing step. Once the three dimensional polymer has been formed it is no longer soluble in water or alcohol. Synthesis condition has to be set to conditions where free phenol and free formaldehyde content of the resin are as low as possible. The free formaldehyde content should not exceed 0.3 to 0.5% and free phenol should not exceed 0.1 to 0.3% (DUNKY and NIEMZ, 2002).

The target viscosities of PF resins largely depend on the desired application. The range starts from 40 to 100mPas for impregnation resins and ends at 1000 to 1800mPas for filling resins for fiber boards which are produced with the wet process. For gluing of massive wood the order of magnitude lies between 1000 to 1500mPas (PECINA et al., 1991).

1.4 Lignins in Phenolic Resins

A lot of research in this field has already been conducted as well as many patents which have been granted. Although a lot of efforts have already been made, no large scale application in industry is known due to technical, economic or process issues as reviewed in MANSOURI et al. (2007). As mentioned above the aim to use natural resources increases with an increased price of the conventional raw material (fossil fuels) for a product.

Due to the fact that lignin is a polyphenolic material (DUNKY and NIEMZ, 2002; PIZZI, 2006; SJÖSTRÖM, 1993) the idea is to substitute a certain amount of solely phenol-based PF resin precondensates by a certain percentage of lignin. This can be accomplished either by adding lignin after the precondensation step as cutting agent, or by implementing it from the beginning into the synthesis. The addition of lignin as cutting agent increase the stickiness in cold conditions and reduces the costs as it can be easily accomplished. However, homogeneous distribution is difficult, and it is so far unknown if the lignin is just a filler or really chemically integrated into the resin. If lignin is present in the reaction mixture already from the beginning of the precondensation step, it can be used unmodified or modified by phenolation or methylation. Phenolation of lignin is performed in acid conditions where lignin and phenol get time to react with each other. This procedure is more of interest for novolac resins because they are as well synthesized under acid conditions. Methylation is operated at alkaline conditions. At this procedure lignin reacts with formaldehyde before phenol is added. Advantage for phenolation and methylation is the increased reactivity of the modified lignin for the later use. Disadvantage is that another process step is introduced which increases the process time (DUNKY and NIEMZ, 2002; ALONSO et al., 2005; MANSOURI et al., 2007).

The approach studied in this master thesis comprises the subsequent addition of lignin, phenol and formaldehyde without the intention of any pretreatment of the lignin. A methylation of the lignin before the actual resins synthesis could have increase the reactivity though also would have increased complexity of the synthesis procedure. If so also the methylation process would have been subject to evaluation and optimization which was not in the scope of this thesis as mentioned in chapter 1.5.

If lignin is used as a phenol replacement, it has to be considered that its number of reactive aromatic ring positions is lower compared to phenol, as both para and partly the ortho positions of phenolic units is blocked by phenylpropan side chains and methoxyl groups, respectively. H-type aromatic units of lignin show the biggest similarity to phenol compared to G-type and S-type aromatic units. Both, the 3rd and the 5th carbon atom position of H-type units are free to react with formaldehyde. Due to the methoxyl group at the 5th carbon atom, G-type units have only one free position at the 3rd carbon atom of the phenolic unit. S-type units have no free aromatic ring position related to the methoxyl groups at the ortho position and due to the phenylpropan side chain at the para position, wherefore it would just function as a cutting agent and could not contribute to the crosslinking (MOHAMAD IBRAHIM et al., 2011). As mentioned above the remaining metal ion after the wood pulping may affect the chemical reactions during the resin synthesis.

1.5 Hypothesis and Goals

It had been hypothesized that adhesives of comparable bonding strength can be obtained if a certain percentage of phenol is replaced by lignin. Therefore lap shear specimens were tested in dry and in wet conditions. For the evaluation of the longitudinal tensile shear strength the null hypothesis H_0 and the alternative hypothesis H_1 were stated:

H_0 : With a significance level of 5% the average longitudinal tensile shear strength of the adhesive groups, of a treatment, is equal.

H_1 : With a significance level of 5% at least one group mean of a treatment is different from the others.

The goal was to develop a procedure for the synthesis of lignin-phenol-formaldehyde adhesives which leads to reproducible adhesives with up to 40% lignin substitution by mass of phenol which have comparable bonding strength. This includes a development of the final formula of the resins, a specific process instruction with all the used instruments and it includes an adjustment of the process till reproducibility was achieved. Afterwards test standards for the characterization of the adhesives

had to be established and applied. Properties in terms of viscosity, solid content, B-time, pH, water miscibility and curing behavior were determined by differential scanning calorimetry. Furthermore the shear strength was evaluated with lap shear specimens as indicator for the bonding strength.

No focus was put on comparison of lignins from different pulping processes (eg.: Organosolv, Kraft, ...) and its effects on bonding strength. The effect of pressing time and temperature on the bonding strength was not evaluated. Also the chemical pretreatment of lignin to increase the reactivity was not investigated as well as an optimization of the molar ratios for the compounds to achieve a faster curing process and lower free formaldehyde content. For a detailed investigation of these impact factors see GHORBANI (2014) and KRAHOFER (2015).

2. Materials and Methods

2.1 Chemicals

Sarkanda grass (*Miscanthus*) Soda lignin (1000-2000 g/mol) and pine Kraft lignin Indulin AT™ (6500-8000 g/mol) (ASIKKALA et al., 2012) were purchased from Granit Technologies SA, Switzerland and Mead Westvaco, Charleston, SC, USA. Phenol (94.11 g/mol; purity ≥ 99.5%) and aqueous formaldehyde solution ($\rho=1.09\text{g/cm}^3$ at 20°C, 30.03 g/mol; 37wt%) were purchased from Carl Roth GmbH & Co. KG, Germany (2013a; 2013b). Sodium hydroxide (39.997 g/mol; purity 97%) was purchased from Sigma-Aldrich Co. LCC (2014). For convenience Sarkanda grass Soda lignin is referred as Sarkanda further on and pine Kraft lignin Indulin AT™ is referred as Indulin in this thesis.

2.2 Adhesive Calculation

The calculations used in this study are based on the Patent WO2009040415 (VAN HERWIJNEN and PROCK, 2009) and on a formulation provided by WIELAND and LIEBNER (2013).

2.2.1 Phenol

WO2009040415 describes the use of 800.00g phenol with a concentration of 90.5%. This result in 724.00g of pure phenol as equation (1) shows.

$$\rightarrow \text{pure phenol} = 800 * 0.905 = 724.00\text{g} \quad (1)$$

The amount of pure phenol divided by the concentration of 99.5% gives a mass of phenol of 727.64g equation (2).

$$\rightarrow \text{phenol with } (c = 99.5\%) = \frac{724}{0.995} = 727.64\text{g} \quad (2)$$

2.2.2 Formaldehyde

1400.00g of a 55.3wt% solution is used in the patent. That is equal to 774.20g of pure formaldehyde, see equation (3).

$$\text{Formaldehyde } (c = 100\%) = 1400 * 55.3\% = 774.20\text{g} \quad (3)$$

For this work a solution of 37 wt% formaldehyde in water was used. The amount of formalin has been calculated according to equation (4).

$$m_{\text{Formalin}} = \frac{774.20 * 100}{37} = 2092.43\text{g} \quad (4)$$

Equation (5) shows the calculation of the formaldehyde : phenol (F/P) ratio as it has been used in one of the examples detailed in WO2009040415. The ratio was adjusted to 2.9 for the screening test (chapter 2.5) and to 2.5 for the reproducibility test (chapter 2.6) and the final adhesives (calculation (6) & (7)). This has been done to reduce the free formaldehyde content in the resin (VAN HERWIJNEN, 2014). The quantities of the chemicals are adapted to a F/P ratio of 2.5. The specific amounts for the screening test with a ratio of 2.9 are listed in chapter 2.5 separately.

$$\frac{mol_{Formaldehyd}}{mol_{Phenol}} = \frac{\frac{m_{Formaldehyd}}{M_{w,Formaldehyd}}}{\frac{m_{Phenol}}{M_{w,Phenol}}} = \frac{\frac{774.2}{30.03}}{\frac{724}{94.11}} = 3.35 \quad (5)$$

$$m_{Formaldehyd} = \frac{mol_{Formaldehyd}}{mol_{Phenol}} * \frac{m_{Phenol}}{M_{w,Phenol}} * M_{w,Formaldehyd} \quad (6)$$

$$m_{Formaldehyd} = 2.5 * \frac{724.00}{94.11} * 30.03 = 577.56g \quad (7)$$

With a 37wt% solution and a formaldehyde : phenol ratio of 2.5 , 1560.97g of formalin are needed, see equation (8).

$$m_{Formalin} = \frac{577.56 * 100}{37} = 1560.97g \quad (8)$$

2.2.3 Sodium Hydroxide

The amount of sodium hydroxide has been calculated according equation (11) based on a molar ratio of 0.12197 (equation (9)) that has been used by WIELAND AND LIEBNER (2013), who described a preparation of a PF pre-polymer. In this approach 1.33g of NaOH were dissolved in 20.3ml of aqueous formaldehyde solution (wt%=37%, $\rho=1.09g/cm^3$ at 20°C). Although the room temperature was around 21°C the density at 20°C was used for the calculations. Thus the calculated amount is lower than the used amount in WIELAND and LIEBNER (2013). This difference was ignored in order to simplify the calculations. Equations (10) and (11) lead to the final amount of sodium hydroxide.

$$\frac{mol_{NaOH}}{mol_{Formaldehyde}} = \frac{\frac{m_{NaOH}}{M_{w,NaOH}}}{\frac{m_{Formaldehyd}}{M_{w,Formaldehyd}}} = \frac{\frac{1.33}{39.997}}{\frac{20.3 * 1.09 * 0.37}{30.03}} = 0.12197 \quad (9)$$

$$m_{NaOH} = \frac{mol_{NaOH}}{mol_{Formaldehyde}} * \frac{m_{Formaldehyd}}{M_{w,Formaldehyd}} * M_{w,NaOH} = \quad (10)$$

$$= 0.12197 * \frac{1560.97 * 0.37}{30.03} * 39.997 = 93.83g \quad (11)$$

The recalculated amount of pure NaOH is 93.83g see equation (11).

2.2.4 Water

	F/P ratio	amount of water
Patent	3.3.....	251.00ml
new ratio	2.5.....	m_{water} ml
$m_{\text{water}} = \frac{2.5 \cdot 251 \text{ml}}{3.3} = 190.15 \text{ml}$		(12)

Compared to WO2009040415 a lower water content is required as the F/P ration was reduced to 2.5 for this study which has been calculated according to equation (12). In the patent a formalin concentration of 55.3% is used. Due to the fact that already more water is in the system – caused by the lower formalin solution of 37 wt% - the amount of added water is adjusted (equation (13)).

	formalin concentration	amount of water
	55.3%.....	190.15ml
	37%.....	m_{water} ml
$m_{\text{water}} = \frac{190.15 \text{ml} \cdot 0.37}{0.553} = 127.23 \text{ml}$		(13)

According to the patent the following amount of water was used for the adhesive synthesis:

phenol (c = 90.5 wt%).....	800 * (1-0.905) = 76.00 g
NaOH (c = 50 wt%).....	44 * (1-0.5) = 22.00 g
formalin (c = 55.3 wt%).....	1400 * (1-0.553) = 625.80 g
<u>water added</u>	<u>251 ml = 251.00 g</u>
total.....	974.80 g

Based on the changed formaldehyde phenol ratio the following amount of water is present in the reaction mixture considered in this study:

phenol (c = 99.5wt%).....	727.64 * (1-0.995) = 3.64 g
NaOH (c = 50 wt%).....	187.66 * (1-0.5) = 93.83 g
<u>formalin (c = 37 wt%)</u>	<u>1560.97 * (1-0.37) = 983.41 g</u>
total.....	1080.88 g

The amount of water according to the above calculation is higher compared to patent WO2009040415. This is due to the fact that a 37wt% aqueous formaldehyde solution had been used which contains more water than the 55wt% aqueous formaldehyde solution did. Although already more water is in the system compared to the patent,

water was added for the screening tests, in order to follow the procedure of the patent. For the reproducibility tests only water which was added in combination with other substances was in the system as mentioned in chapter 2.5 and 2.6.

2.2.5 Lignin

The used amounts of lignin were calculated based on the mass of used phenol and the desired degree of phenol substitution (Table 2 and Table 3).

2.3 Experimental Setup

A hotplate RCT basic (IKA®-Werke GmbH & CO. KG, Staufen, Germany) with an adapter for round bottom flasks and one glass encapsulated temperature sensor (accuracy 1°C) was used. During the reproducibility tests the temperature sensor was replaced by an ETS-D5 contact thermometer (IKA®-Werke GmbH & CO. KG, Staufen, Germany) with a proportional-integral-derivative-controller (PID). This thermometer had an accuracy of 0.1°C and due to the PID controller the temperature can be controlled more accurate. Due to the strongly alkaline conditions all temperature sensors had to be glass encapsulated according to the operating instructions of the devices. The temperature sensor was installed through one of the side openings of the three neck round bottom flask. The other side opening was used to connect a dropping funnel for the addition of formalin (Figure 8). During the reproducibility tests the dropping funnel was replaced first by a peristaltic pump Reglo Analog MS-4/12 (IDEX Health & Science GmbH, Wertheim, Germany) and later on by a titration device Titro Line 7000 (SI Analytics GmbH, Mainz, Germany) in order to ensure a constant volume flow (Figure 9). A reflux condenser was connected to the flask using the central opening to prevent formaldehyde from evaporation.

When the addition of formalin was completed the used device was removed and the side opening closed with a glass stopper. Although all openings of the round bottom flask were used, the top opening of the reflux condenser remain opened to have an opened system. To weigh all the compounds a scale with an accuracy of 0.01g was utilized.



Figure 8: Experimental setup 1

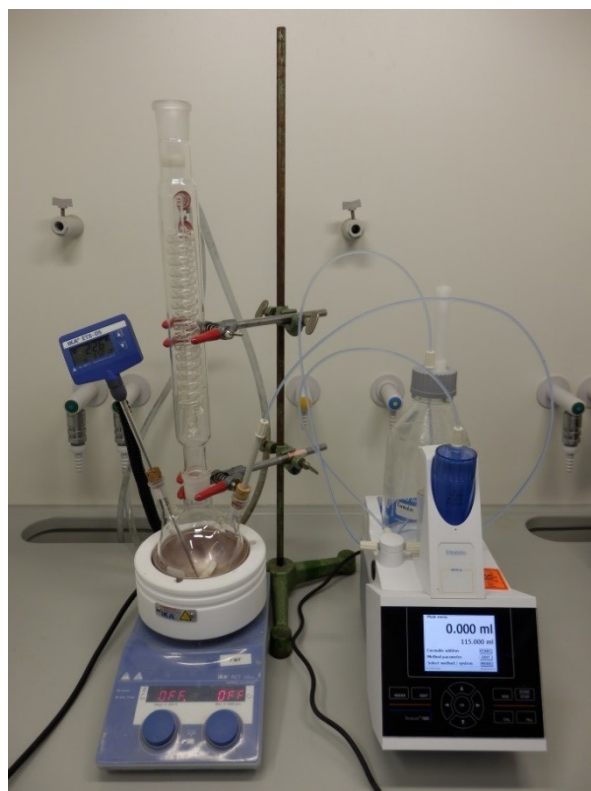


Figure 9: Experimental setup 2

2.4 Procedure

For the screening tests (chapter 2.5) first solid phenol and afterwards lignin were added into a three neck round bottom flask. Subsequently the 50 wt% solution NaOH was added. To guarantee a constant mixing a stirring bar was added into the flask and operated at 160rpm.

Due to the exothermic reaction between phenol and sodium hydroxide which could easily reach 60°C, phenol (melting temperature 41°C) started to melt. Furthermore the reaction between NaOH and phenol is leading to the formation of water which dissolving sodium phenylate. After the exothermic reaction stage had declined the temperature of the hotplate was set to 65°C. At the point this temperature was reached formalin was added with a dropping funnel and the rate of formalin addition was controlled by opening and closing the dropping funnel manually. The reaction between phenol and formalin is much more exothermic than between phenol and NaOH, which is why the addition of formalin was stopped from time to time to keep temperature peak below 80°C.

From the point on when all ingredients were mixed together the temperature was increased to target temperature (80°C) and after one hour the viscosity measurements were started at an interval of 30 minutes. Time and temperature were recorded at each point when an ingredient was added or a sample for the viscosity

measurement was extracted. When the target viscosity was reached the flask was removed from the hotplate and put into a water bath to cool down the adhesive to room temperature upon continued stirring. Afterwards the adhesive was transferred to a plastic bottle and stored in a fridge. According the order of magnitude of viscosities (chapter 1.3) the target viscosity was set to 1000mPas which turned out as most practicable for the preparation of lap shear samples.

For the reproducibility tests (chapter 2.6) the sequence of the addition of the chemicals was changed. In the final procedure first lignin, second phenol, afterwards sodium hydroxide and then formaldehyde was added into a three neck round bottom flask. It turned out that this order of adding the chemicals greatly simplifies handling, as sometimes lignin dust got stuck at the upper inner walls of the reaction flask and could hardly removed without losing some of the phenol too. In case a resin without lignin was produced the order stayed the same except no lignin was added.

Till resin t14 formalin was added within a dropping funnel which was opened and closed manually to control the temperature increase. During the addition the dropping funnel was controlled by hand. It was opened and closed depending on the temperature development of the resins to avoid a temperature overshoot with the objective to enter all the formalin within a set time frame. The dropping funnel was only opened that much that the formalin entered the flask dropwise, so the speed was adjusted subjective. To assure a more constant volume flow of formalin the dropping funnel was replaced by a peristaltic pump (Table 8). Hence, resins t15 and t16 were produced with a peristaltic pump. Later on it was replaced by an automatic titration device for resins t17 to t19. With both, the peristaltic pump and the titration device a defined volume flow was adjusted which is essential with regard to reproducible formalin addition and characteristics of the final adhesive.

The set time frame for the addition of formalin at the screening test was 10 to 12 minutes and for the reproducibility test resins t01 to t07 10 minutes. Due to the increased amount of formalin, as a result of the optimization efforts, the duration of formalin addition was increased to 25 minutes for resins t08 to t16. For the test resins t17 to t19 the time frame was reduced to 15 minutes.

2.5 Screening

The screening tests had the purpose to investigate the impact of lignin on the viscosity of the reaction mixture with the aim to stop the synthesis at a target viscosity of 1000 to 2000mPas. The first approach was to find a synthesis temperature to achieve the target viscosity within an acceptable time frame of 2 to 3 hours. The target temperature for the first adhesive was set to 65°C, increased to 90°C for the second adhesive and finally the synthesis was performed at 80°C. Secondly the impact of both Sarkanda and Indulin on the viscosity development at phenol substitution levels of 0, 5, 10, 15, 20, 25, 30 and 40% was tested.

For the screening tests just a small amount of the above calculation was used and the F/P ratio increased to 2.9. The amounts were scaled to 1.5% of the calculations made in chapter 2.2:

phenol (c = 99.5wt%).....	727.64 * 0.015 = 10.91 g
NaOH (c = 100%).....	93.83 * 0.015 = 1.41 g
Water.....	127.23 * 0.015 = 1.91 g
<u>formalin (c = 37 wt%)</u>	<u>1560.97 * 0.015 = 23.41 g</u>
total.....	37.64 g

The upper values were changed to a F/P ratio of 2.9 using the following amounts:

phenol (c = 99.5wt%).....	10.80 g
NaOH (c = 100%).....	1.50 g
water.....	1.91 g
<u>formalin (c = 37 wt%)</u>	<u>26.70 g</u>
total.....	40.91 g

The amount of added lignin was calculated by mass for 0, 5, 10, 20, 30 and 40% of the used amount of phenol (Table 2). The sodium hydroxide was added as a 50wt% solution. Thus 1.50g of NaOH was added with 1.50g water. In total 1.91g of water have to be added to the flask. Therefore the missing amount of water had to be added which was 0.41ml.

Table 2: Amounts of phenol and lignin for the different lignin substitution levels

Lignin substitution level	[%]	0	5	10	15	20	25	30	40
Phenol	[g]	10.80	10.26	9.72	9.18	8.64	8.10	7.56	6.48
Lignin	[g]	0	0.54	1.08	1.62	2.16	2.70	3.24	4.32

2.6 Reproducibility

After finishing the screening tests, the procedure was checked for reproducibility which was evaluated by viscosity of the formed pre-condensate at a certain cooking time. To ensure good handling for further processing, such as curing, an acceptably low viscosity of 1000 mPas was targeted. For this purpose, pre-condensates (adhesives) containing 20% Sarkanda analysed for their viscosity at different stages of the cooking process.

As temperature greatly affects the step-growth polymerisation rate, this parameter was recorded every five minutes, starting at the time when the addition of formalin was completed. During the addition of formalin with the dropping funnel, the volume flow was manually adjusted to control the fast temperature increase due to the exothermic reaction. Hence, the volume flow within a resin group was not uniform. Table 3 shows the used amounts of chemicals for the test resins t01 to t19. Resins t01 to t07 were prepared with 1.5% of the in chapter 2.2 described amounts of substances and from resin t08 the scale was increased to 8%. The reasons for the change in scale will be pointed out in chapter 3.2 “Reproducibility Tests”.

Table 3: Used amounts of substances for the reproducibility tests

Declaration [1]	Phenol [g]	Lignin [g]	50wt% NaOH solution [g]	Formalin [g]	Total [g]
t01-t07	8.73	2.18 (20%)	2.81	23.41	37.14
t08-t09	58.21	0 (0%)	15.01	124.88	198.10
t10-t14	46.57	11.64 (20%)	15.01	124.88	198.10
t15-t16	46.74	11.68 (20%)	15.07	125.35	198.84
t17-t19	46.74	11.68 (20%)	15.07	125.35	198.84

The time allowed for the addition of formalin was constant within the different groups of resins for all reproducibility tests. It was 10 min for resins t01-t07 while 25 min for t08-t016 and 15 min for t017-t019. The general procedure and changes for each group are listed in Table 4 to Table 9.

Table 4: Overview of the procedure and equipment for the resins t01 - t05

Resins t01 - t05	
Order of adding chemicals	Equipment
8.73g phenol	IKA hotplate
2.18g lignin	IKA standard temperature sensor
2.81g 50wt% aq. NaOH solution	dropping funnel
23.41g formalin	rheometer without temp. control unit

From resin t06 a contact thermometer ETS-D5 which is equipped with a proportional-integral-derivative-controller (PID) was used to reduce the temperature fluctuations during the adhesive synthesis (Table 5).

Table 5: Overview of the procedure, equipment and changes for resins t06 - t07

Resins t06 - t07	
Order of adding chemicals	Equipment
8.73g phenol	IKA hotplate
2.18g lignin	contact thermometer IKA ETS-D5
2.81g 50wt% aq. NaOH solution	dropping funnel
23.41g formalin	rheometer without temp. control unit
difference to previous approach in Table 4	
contact thermometer IKA ETS-D5	

Apart from the temperature sensor ETS-D5, other changes related to the total amount of resin which was increased as described above, and the amount of added lignin which was zero for the resins t08-t09 (Table 6).

Table 6: Overview of the procedure, equipment and changes for resins t08 - t09

Resins t08 - t09	
Order of adding chemicals	Equipment
58.21g phenol	IKA hotplate
0g lignin	contact thermometer IKA ETS-D5
15.01g 50wt% aq. NaOH solution	dropping funnel
124.88g formalin	rheometer without temp. control unit
differences to the previous approach in Table 5	
total amount was increased	
no lignin in this approach	

Table 7: Overview of the procedure, equipment and changes for resins t10 - t14

Resins t10 - t14	
Order of adding chemicals	Equipment
46.57g phenol	IKA hotplate
15.01g 50wt% aq. NaOH solution	contact thermometer IKA ETS-D5
11.64g lignin	dropping funnel
124.88g formalin	rheometer without temp. control unit
differences to the previous approach in Table 6	
NaOH solution was added before the lignin	
lignin was again added	

After resins with bigger amounts of chemicals and without lignin were synthesized the procedure was changed for resins t10 to t14 as noted in Table 7. For the change to the peristaltic pump the amount of formalin was converted from g to ml. The added amount of formalin could be better controlled by the volume flow than by mass. The volume flow was dependent of the rotations per minute and of the cross section of the used tube. With the known volume flow and a defined time the needed volume was added. Therefore, the mass of formalin (124.88g) was divided by its density ($\rho=1,09\text{g/cm}^3$) which resulted in a volume of 114.58ml. To simplify the handling the volume was increased to 115ml (125.35g). Hence all amounts of substances had to be adjusted to fulfill the F/P ratio and the NaOH/F ratio with the quotient of 125.35g divided by 124.89g (Table 8).

Table 8: Overview of the procedure, equipment and changes for resins t15 - t16

Resins t15 - t16	
Order of adding chemicals	Equipment
46.74g phenol	IKA hotplate
15.07g 50wt% aq. NaOH solution	contact thermometer IKA ETS-D5
11.68g lignin	peristaltic pump
115ml formalin	rheometer without temp. control unit
differences to previous approach in Table 7	
formalin was measured volumetrically therefore the total amount was adapted	
peristaltic pump to add formalin	

The addition of formalin was finally changed to an automatic titration device for resins t17 to t19 and the lignin was placed into the flask before the phenol and the sodium hydroxide was added. Furthermore a rheometer with temperature control unit was used for the viscosity measurements (Table 9).

Table 9: Overview of the procedure, equipment and changes for resins t17 - t19

Resins t17 - t19	
Order of adding chemicals	Equipment
11.68g lignin	IKA hotplate
46.74g phenol	contact thermometer IKA ETS-D5
15.07g 50wt% aq. NaOH solution	titration device
115ml formalin	rheometer with temp. control unit
differences to previous approach in Table 8	
first of all lignin was put into the flask	
titration device to add formalin	
rheometer with temperature control unit	

2.7 Adhesives for Lap Shear Tests

After an optimized standard procedure was defined, a set of adhesives was prepared. Resins with Sarkanda contents of 5, 10, 20, 30 and 40% were produced as well as one pure phenol formaldehyde reference adhesive to see if there is a difference between the lignin modified adhesives and the pure one. To eliminate the factor of storage time only two resins were produced, characterized and used to produce lap shear specimens per week. Hence, every two days one new resin was synthesized and the day between was used to make the characterization tests

2.8 Characterization of PF and LPF Adhesives

Five characterization tests were accomplished for every adhesive. The parameters viscosity at certain points during the resin synthesis, B-time as a value for the curing behavior, solid content, water miscibility as a criterion for the progress of the condensation of the resin as well as pH at the end of the synthesis process were determined. Furthermore, differential scanning calorimetry was performed to determine the differences in curing mechanisms between the adhesives.

While the viscosity measurements were performed directly during the synthesis, all other tests were carried out the day after due the few remaining hours after the adhesive production. To see how viscosity and water miscibility is changing over time, both parameters were determined again after two weeks.

2.8.1 Viscosity Measurement

Viscosity has been used as the main parameter to monitor the synthesis of the adhesives. One hour after completion of the addition of all reactive chemicals the first sample for the viscosity determination was extracted from the flask and performed.

All screening tests and part of the reproducibility tests were conducted in a rheometer of the type Bohlin CVO (Malvern Instruments Limited, Malvern, UK) without an automated temperature control unit which had a conical rotating plate (\varnothing 40 mm, 4°). A plastic pipette tip was used to transfer 3 to 4ml of the respective adhesive from the flask to a 50ml beaker. Subsequently, 1.2-1.3 ml of the adhesive were transferred onto the object carrier of the rheometer using a 3ml syringe connected to a wide-bore cannula (0.8mm). The adhesive sample was not extracted directly with the syringe due to the fact that the cannula was too short to reach the resin in the flask. Furthermore the amount of adhesive could be positioned more precisely with the syringe than with the pipette. To report the temperature of the resin a portable electric thermometer (PT100) with an accuracy of $\pm 2^{\circ}\text{C}$ was used. The latter consists of two wires of different metals twisted together whose different thermal expansion lead to

mechanical stress dependent on the respective temperature. The temperature measurement of the adhesive sample was accomplished by dipping the PT100 into the adhesive sample which was on the object carrier of the rheometer. After the needed amount of adhesive was applied and the sample had room temperature the test was started. The conical plate of the rheometer started to rotate when it arrived at a distance of 0.15mm to the object carrier.

During the development of the synthesis process in the reproducibility test an identical rheometer of type Bohlin CVO (Malvern Instruments Limited, Malvern, UK) with an automatic temperature control unit and a conical rotating plate could be used, which was able to cool down the adhesive sample and to hold the temperature with an accuracy of 0.1°C. The rheometer without automatic temperature control unit was used for all screening tests and till resin t16 of the reproducibility test because the other device with the automatic control unit was simply not available in the beginning.

The temperature was set to 20°C, shear rate 200s⁻¹, time between measuring points (integration time) 10s, waiting time 3s, delay time 1s and number of data points 10.

2.8.2 Solid Content

Solid content (SC) has been determined according to ISO 3251 (2008). To that aim two petri dishes of glass were used. The dishes had an inner diameter of base of 75mm and a rim of 5mm. For a divergent size of the dishes the amount of resin has to be adapted according to the standard. Before use the dishes were degreased with acetone and cleaned with water. The dishes were dried in an oven at 103±2°C for better precision and stored in a desiccator until use.

For this size of dish the amount of resin according to the standard is 3±0.5g. The used scale had an accuracy of 0.1mg. First the mass of the empty dish was measured (m_1). In the second step approx. 3g of resin were filled in and the mass of the dish including the resin was determined (m_2).

According to ISO 3251 liquid phenolic resins have to be dried for one hour at 135°C in a ventilated oven. To assure a constant weight the heating period was extended to 16 and 24 hours. Therefore, all samples were dried for 16 hours, then weighed (m_{16}) and dried till a duration of 24 hours was completed (m_{24}). Due to the workflow the solid content after 16 hours (SC₁₆) was needed to calculate the adhesive application quantity for the gluing of the beech boards of which the lap shear samples were made out of. To monitor if the solid content after 24 hours (SC₂₄) is different the samples were dried for 8 more hours. The solid content SC_{16/24} was calculated according to equation (14).

$$SC_{16/24} = \frac{m_{16/24} - m_1}{m_2 - m_1} * 100 [\%] \quad (14)$$

2.8.3 B-Time

B-Time according to DIN 16916-2 (1987) investigates the curing rate of a resin using a B-Time plate whose central indentation has calotte-type geometry (Ø 25 mm, 5mm depth).

As a B-Time plate according to DIN 16916-2 was not available for the conducted work, a substitute had been made from a 1cm thick aluminium plate. Instead of implementing a calotte-shaped hole which would have required a ball cutter (Ø 25mm), a countersink with a radius of 5.5mm at the base and an angle of 45° was used. The final hole had hence the geometry of a frustum of a cone with a diameter of 11mm at the bottom of the indentation, a basic diameter of 20.5mm and a depth of 5mm. Beyond that, the surface roughness of the substitute B-plate did not achieve the specifications required according to DIN 16916-2. However, polishing of the plate with grain 1000 sand paper was accomplished to make the measurements better comparable. Equations (15) to (20) were performed to reveal the differences regarding volume and surface caused by using the substitute B-plate.

Calotte	Frustum of a cone
Volume	Volume
$V = \frac{h^2\pi}{3}(3r - h) =$	$V = \frac{h\pi}{3}(R^2 + R * r + r^2) =$
$V = \frac{5^2\pi}{3}(3 * 12.5 - 5) =$	$V = \frac{5\pi}{3}(10.25^2 + 10.25 * 5.5 + 5.5^2) =$
$V = 850.8mm^3$	$V = 1003.7mm^3$
(15)	(16)

$$\frac{V_{Frustum\ of\ a\ cone}}{V_{Calotte}} = \frac{1003.7}{850.8} = 1.179 \rightarrow +18\% \text{ more volume} \quad (17)$$

Surface	Surface
$A = 2 * h * r * \pi =$	$A = (R + r) * \pi * m + \pi * r^2 =$
$A = 2 * 5 * 12.5 * \pi =$	$A = (10.25 + 5.5) * \pi * 6.89 + \pi * 5.5^2$
$A = 392.7mm^2$	$A = 436.0mm^2$
(18)	(19)

$$\frac{A_{Frustum\ of\ a\ cone}}{A_{Calotte}} = \frac{436.0}{392.7} = 1.110 \rightarrow +11\% \text{ more surface} \quad (20)$$

The B-Time was determined at 130°C (DIN 16916-2). Beyond that, B-time was also measured at 100°C to simulate the temperature required for hot pressing of beech boards used in lap shear testing.

A syringe and a connected canula were rinsed with adhesive and then weighed empty. Subsequently 0.5g were weighed in the syringe. For the test glass sticks with a tip diameter of 2mm were needed. Therefore the tips of glass pipets were melted with a Bunsen burner in order to fulfill the requirements for the test.

To heat up the B-Time plate a controlled heating element of the ABES (Automated Bonding Evaluation System) device was used. The B-Time plate was mounted with copper wires onto the heating element which had an accuracy of $\pm 1^\circ\text{C}$ (Figure 10). The temperature sensor was located in the heating element of the ABES under the B-Time plate.

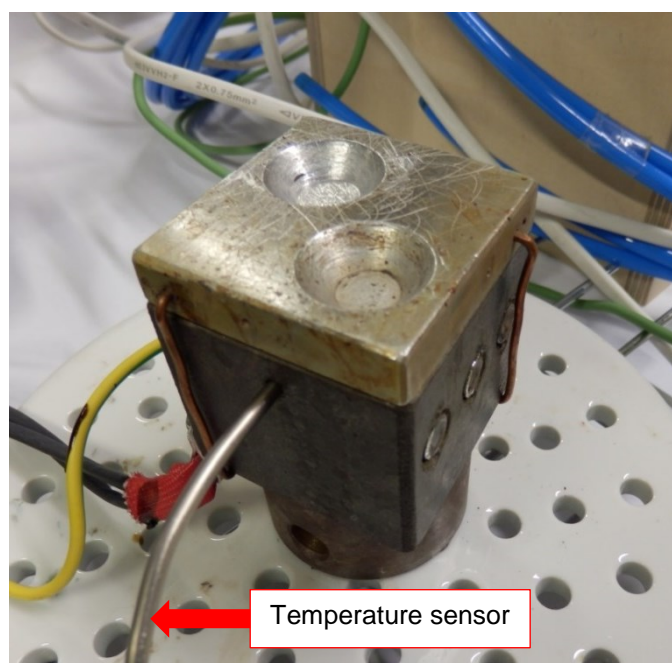


Figure 10: B-time plate mounted onto the heating element of an ABES

After the heating element had reached the target temperature, five more minutes were waited to ensure full heat transfer to the B-Time plate before the resin sample of 0.5g was placed into the conical mould ($t=0$). The prepared pipet was used to stir the resin sample directly after it was placed into the mould. The stirring had to be continued during the first minute, followed by a one minute break, subsequently 10 seconds of stirring which was again followed by a one minute break. The cycle 1 minute break 10 seconds of stirring was continued until the resin became more viscous. The stick had to be pulled out from time to time to check if the filaments of the resin are breaking which is an indicator for a cured polymer. When the filaments are breaking the curing of the adhesive is completed and the B-Time is recorded. As

the curing of the resin got more advanced the resin sample became pasty and the stirring had to be continued without any break in order not to miss the B-Time. The B-Time was reached when during short pullouts during stirring phase the filament broke. For each of the tested temperature levels two samples were tested. If the difference of the two samples was more than 10% the test was repeated.

2.8.4 pH-Value

The pH-value was determined at room temperature immediately after the resin was filled into a storage bottle using a GMH 5550 electrode (Greisinger Electronic GmbH, Regenstauf, Germany).

2.8.5 Water Miscibility

Water miscibility (WM) was determined according to standard ISO 8989 (1995). Depending on its degree of condensation, the water miscibility of the obtained resins can significantly vary. Older resins have a lower miscibility than newer ones.

5 g of the adhesive were placed into a 150 ml beaker and gently stirred using a magnetic bar. Subsequently deionized water was slowly added using a 50 ml burette until the resin turned turbid. Water miscibility is expressed as a percentage of added water volume (V) in ml by mass (m) of the test portion in g as equation (21) shows.

$$WM = \frac{V}{m} * 100 [\%] \quad (21)$$

For samples that required the addition of water in volumes larger than 100 ml, the whole content of the 150ml beaker was transferred to a 1000ml beaker before the amount of added water was increased to altogether 600 ml. In case the sample did not turn turbid at this stage, the volume was increased to 1000ml. If even at this high degree of dissolution the sample remained clear, the respective resin was classified as infinitely good water soluble.

2.8.6 Differential Scanning Calorimetry (DSC)

All DSC measurements were performed for sets of three identical samples using a DSC 200 F3 Maia (NETZSCH-Gerätebau GmbH, Selb, Germany). 20µg to 30µg of the respective samples ($\pm 0.001\mu\text{g}$) was weighed into a gold coated high pressure crucible and placed onto the DSC sample holder. An empty crucible served as reference. Both vessels were sealed with a torque of 2Nm with gold coated caps capable of resisting a pressure of 2 MPa. The following temperature program was used: 20°C, 10°C·min⁻¹ to 250°C. Cooling after the measurement was accomplished with liquid nitrogen. For each resin three samples were tested.

2.8.7 Free Formaldehyde Content

Free formaldehyde content was determined in triplicate for each of the resins following the ISO 11402 protocol and using the titration device Titro Line 7000 (SI Analytics GmbH, Mainz, Germany).

2.9 Preparation of Lap Shear Samples

The preparation was based on the standard ÖNORM EN 302-1 (2004). After an adhesive was synthesized and characterized, it was used to produce lap shear samples with thin adhesive layer for the determination of the longitudinal tensile shear strength.

2.9.1 Geometry and Wood Species

The lap shear samples had a size of 150mm x 20mm in plan and a thickness of 10mm according to the standard. For this purpose two 5mm thick planed boards of beech (*Fagus sylvatica*) were glued together and cut to the described dimensions. All of them had one perpendicular cut of approx. 3mm on each side which was shifted asymmetrical from the center to create an overlapping area of 10mm length in the center of the sample (Figure 11).

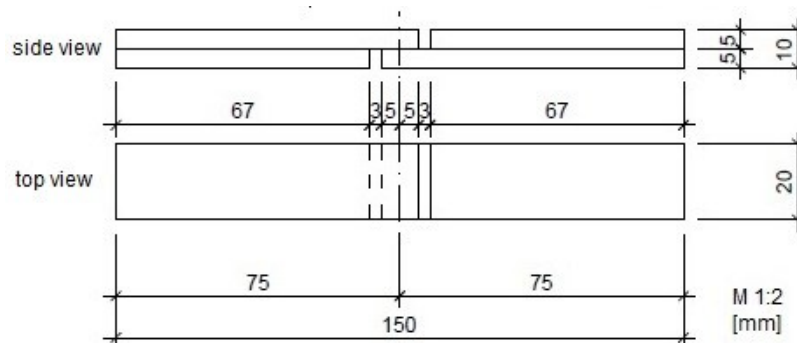


Figure 11: Dimensions of a lap shear sample

2.9.2 Preparation of Boards

The beech boards were made out of two three meter long and 50mm thick poles which were cut to 50cm long pieces with a width of approx. 15cm and split to 10mm boards. Subsequently the boards were numbered and stored in a climate room at 20°C and a humidity of 65% to reach the target moisture of 12±1%. To guarantee good drying conditions the boards were stacked using thin sticks to improve air circulation and clamped together in order and to reduce warping.

The length of 50cm was chosen as the used press had a maximum operational area of 50cm by 50cm. Widthwise three board pairs could be put into the press. One

board pair had dimensions of about 15cm by 50cm, which guarantees to cut out 5 stripes of 20mm including all the losses due to cutting. One stripe was cut to three 150mm long specimens. Following the above-described cutting schema, 15 samples could be obtained for each pair of glued beech wood boards. For each adhesive three glued board pairs for lap shear samples was pressed which leads to a total amount of 45 samples per resin and pressing cycle (Figure 12). The surfaces of the boards were planed to a thickness of 5mm at the earliest 24h before they were glued together as described in the standard.

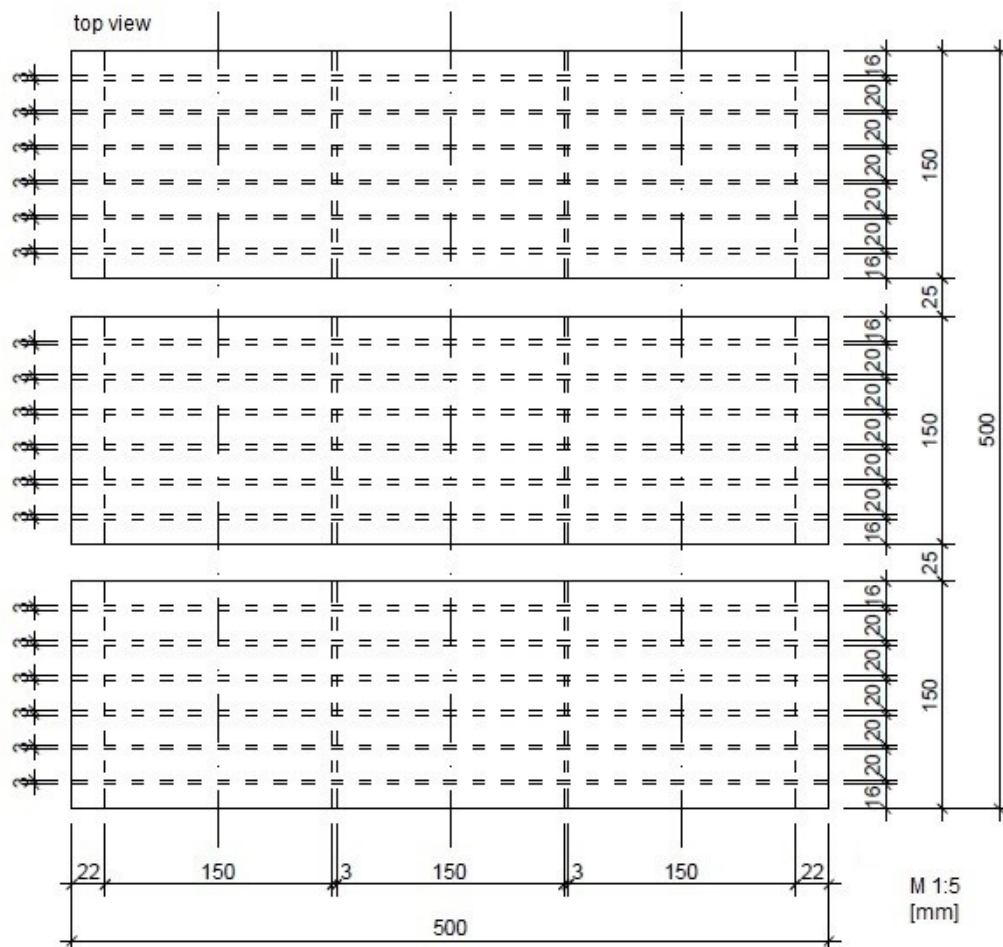


Figure 12: Cutting pattern for three board pairs

2.9.3 Wood Moisture and Density

At this stage the boards were selected randomly to reduce the density influence of the two poles. The standard requires a density of $0.7 \pm 0.05 \text{ g/cm}^3$ and a moisture of $12 \pm 1\%$ of each board.

To determine the density and the wood moisture according to the oven-dry method a sample of 10mm width of the length was cut from one edge of each board. The

dimensions of the samples were measured using a vernier caliper with an accuracy of 0.01mm and were approx. 150mm x 10mm x 5mm. Mass of the samples was determined with a scale which had an accuracy of 0.01g. By dividing mass by volume the density of the standard climate conditioned samples was obtained.

The moisture content of the boards was analysed with the moisture meter Hydromette M 4050 (GANN Mess- und Regeltechnik GmbH, Gerlingen, Germany) functioning by the principle of electrical resistance (w_{el}). The electrodes were hammered into the wood transvers to the direction of the fibers. Before measuring the wood moisture the wood species and the wood temperature had to be adjusted at the device. The used device requires a minimum board thickness of 10mm which was ignored due to the board thickness of 5mm. This method was performed since the oven-dry method takes more time and it was necessary to check if the moisture was in the target range before the boards were glued together.

The oven-dry method was performed to obtain a precise result of the wood moisture. Therefore, the samples from the density determination were used to determine the moisture (w_{oven}) with the oven-dry method through drying till they reach a constant weight. They were put into an oven which had a temperature of $103\pm 2^\circ\text{C}$ and a ventilation system. The samples were at least 2 days or longer in the oven to reach constant weight. When the samples were weighed, they were put out of the oven and stored in a desiccator which was filled with silica gel to prevent the samples from absorbing water from the air and to cool down to room temperature. Afterwards the mass was measured ($\pm 0.01\text{g}$). The samples were put back into the oven and measured again at the moment when the next group of samples was measured. When the mass did not change by more than 0.01g, the weight of the sample (m_0) was used to calculate their moisture content.

$$w_{oven} = \frac{m_w - m_0}{m_0} * 100 [\%] \quad (22)$$

In equation (22) the mass of the wet sample (m_w) and the mass of the sample with 0% moisture (m_0) is used to calculate the amount of water in the sample (numerator) which is related to the dry mass (m_0) of the sample (denominator).

2.9.4 Gluing and Pressing

After determining their density and moisture, the boards were matched by the criteria of density. To prevent that two very dense boards were assigned the board with the highest and the board with the lowest density were put together. In the next step the board with the second highest density and the second lowest density were matched together and the two remaining boards formed a pair. The requirement of the

standard that the boards which are pressed together have to be out of one pole was not fulfilled.

To heat up the hotplates of the press, the boiler was set to 160°C and the hotplates to 120°C. It was necessary to calculate the contact area of the board pairs to determine the amount of needed resin. LOH et al. (2011) suggest an adhesive spread rate of 200g/m² for an urea formaldehyde (UF) resin of 42.5% solid content for plywood gluing whereas GASPAR et al. (2009) proposed an adhesive spread rate of 500g/m² for a phenol resorcinol formaldehyde (PRF) resin for laminated timber. As mentioned before the samples are later on used as lap shear samples which have to be processed in a very specific way avoiding any surface irregularities as mentioned in chapter 2.9. For the use of lap joints according ÖNORM EN 302-1(2004) literature claims a spread rate of 200 to 300g/m² (KONNERTH et al., 2006; KONNERTH et al., 2014). Hence and also due to the higher solid content of the synthesized adhesives (chapter 3.3) an adhesive spread rate of 200 g/m² was chosen for the production of lap shear samples. The needed amount of resin was calculated based on the selected adhesive spread rate and the contact area. With the data of the solid content of each resin, the amount of solid resin per square meter was calculated. For the final adhesives which are used for gluing of the beech boards it was important to apply the same mass of solid resin. Combined with the solid content the wet mass for each resin could be calculated.

For example:

A board has an area of 0.075m² (0.15m x 0.50m). Assuming a fixed amount of adhesive of 200g/m², the applied mass for this board is 15.0g. If the resin has a solid content of 50% the solid adhesive spread rate is 100g/m².

If the next board has a surface of 0.06m² (0.12m x 0.5m) and the used resin a solid content of 45%, the spread rate is 222g/m² (100/0.45) and the absolute mass is 13.32g for that board.

Pressing pressure and time were also calculated and entered into the operating program. The area of gluing surfaces of all three board pairs were known and also the total area of the press (0.5m by 0.5m). For the total area the maximum pressure was 0.8MPa. This value was low enough to ensure that the compressive strength is not reached and to apply enough pressure to press the boards together. The actual contact area of the boards was divided by the press area to determine how much area of the press is used. This factor was multiplied with the maximum pressure and led to the actual pressure.

For calculation of the required pressing time, B time at 100°C was multiplied by the safety factor 2. A safety factor of 2 was set to guarantee a complete hardening of the

adhesive in case the temperature in the glue layer was not 100°C. Additionally a heating-up time for the boards was included into the calculations which was set to one minute per mm of board thickness. For two 5mm thick boards a heating time of 5 minutes was calculated, see equation (23).

$$\text{Pressing time} = 2 * (B - \text{Time}_{100^{\circ}\text{C}}) + 1\text{min/mm} \quad [\text{min}] \quad (23)$$

The closing speed of the press was set to maximum performance until a plate-to-plate distance of 20mm was reached and then reduced to 20mm/min.

A scale with an accuracy of 0.01g was used to weigh the amount of resin to be applied on the respective boards. For this purpose, the boards were placed onto the scale which was then set to zero. Now, the adhesive was applied with a one way pipet and distributed with a toothed spatula. It was important that the surface was consistently wet with adhesive. In order to assure that the needed quantity of resin was applied the boards were placed on the scale several times to determine the weight of the applied adhesive. Prior to pressing the surrounding workspace was covered with paper to prevent it from pollution with adhesives. After all pairs were ready they were put into the press and the press was activated. The pressing time started when the press was closed and reached the set pressure. When the time was over the press opened automatically.

2.9.5 Storage Conditions for the Specimens

Immediately after the pressing was finished, the boards were stacked with sticks and clamped together in the climate room. They were clamped together in warm conditions to reduce warping during cooling down. According to the standard, the glued boards have to be cut to samples after three days of storage at 20°C and 65% humidity (standard climate).

The lap shear specimens were divided into two treatments. Treatment A1 and A2 according to the standard were chosen. For treatment A1 the samples were stored for seven days under standard conditions (20°C and 65% humidity) and the testing of them immediately afterwards. A2 describes the storage for four days under water and then testing the samples in wet conditions. Treatment A1 was adapted to a storage time of at least seven days or more in the climate room (A1+). Due to the fact that all board pairs were cut to samples at once and due to their different production date, the first boards stayed some weeks in the climate room before they were processed. On the other hand the last boards which were produced resided just the prescribed time under standard conditions. The EN ÖNORM requirements for treatment A2 were fulfilled. According to the standard at least ten valid samples had to be tested per

condition. To have enough samples, 20 samples of each resin were stored in water (A2) and the other 25 samples of each resin were stored in the climate room (A1+).

2.10 Lap Shear Tests

The test was performed according the ÖNORM EN 302-1 (2004). All samples were tested during one day. The test was carried out with a testing machine Z020 (Zwick GmbH & Co. KG, Ulm, Germany). The distance between the chuck jaws was 70mm, applied pre-force before testing was 50N which was set with a speed of 10mm/min. The samples were tested at a speed of 0.7mm/min to ensure a duration of 30 to 90s according to the standard.

The results are shown with a boxplot. The boxplot displays the box with the 25.percentile (first quartile), 50.percentile (second quartile = median) and the 75.percentile (third quartile). The difference between first and third quartile is called interquartile range (IQR) which is used to construct the whiskers. The distance between the box and the whiskers is 1.5 times the IQR. Every value which lies outside this range is considered to be an outlier.

Statistical analysis of the data was accomplished by one way ANOVA for a significance level of 5% (H_0 and H_1). A Scheffé-Test was conducted to determine which group averages differ and which groups do not. For inhomogeneous variances, a Tamhane test was performed. The test of normal distribution was achieved with a Shapiro Wilk test.

H_0 : With a significance level of 5% the average longitudinal tensile shear strength of the groups is equal.

H_1 : With a significance level of 5% at least one group mean of a treatment is different from the others.

3. Results and Discussion

3.1 Screening Test

The results show the development of viscosity for the first four resins s01-s04 (Figure 13). The synthesis for resin s01 was stopped after more than six hours due to the fact that viscosity increased extremely slowly. Therefore the synthesis temperature was increased to 90°C for the second resin (s02). As displayed in Figure 13 the viscosity increased too fast for a controllable process and reached 8000mPas after 90minutes. Hence, the temperature was decreased to 80°C for the resins s03 and s04. With this adjustment the target viscosity of 1000mPas to 2000mPas was reached within acceptable time limits. Consequently, all resins were synthesized at 80°C.

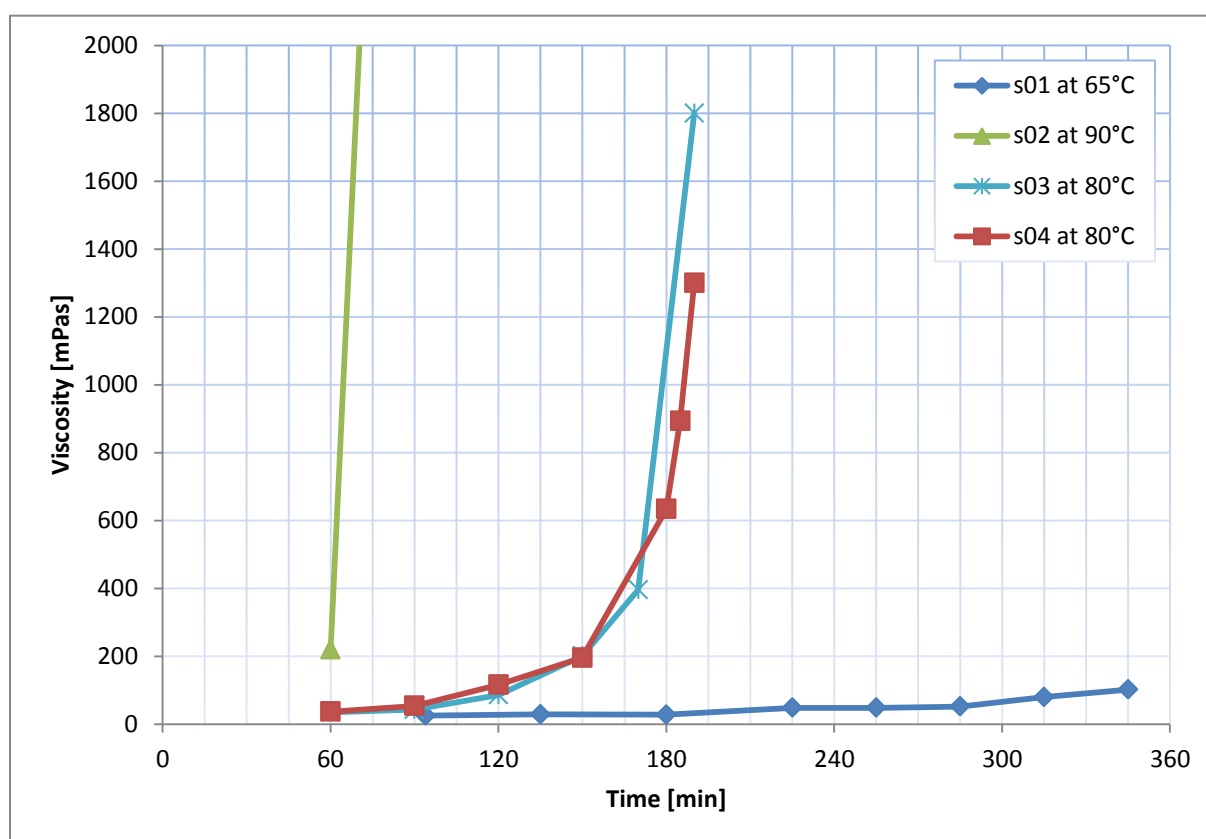


Figure 13: Viscosity trend for resins s01 to s04 over time and varied temperatures

As mentioned in chapter 2.4 the next step included the substitution of phenol by Sarkanda lignin. The impact of lignin on the viscosity is illustrated in Figure 14. Adding Sarkanda lignin led in general to a faster development of viscosity. Resin s07 with 20% Sarkanda lignin was the fastest curing adhesive, followed by resin s09 with 40%.

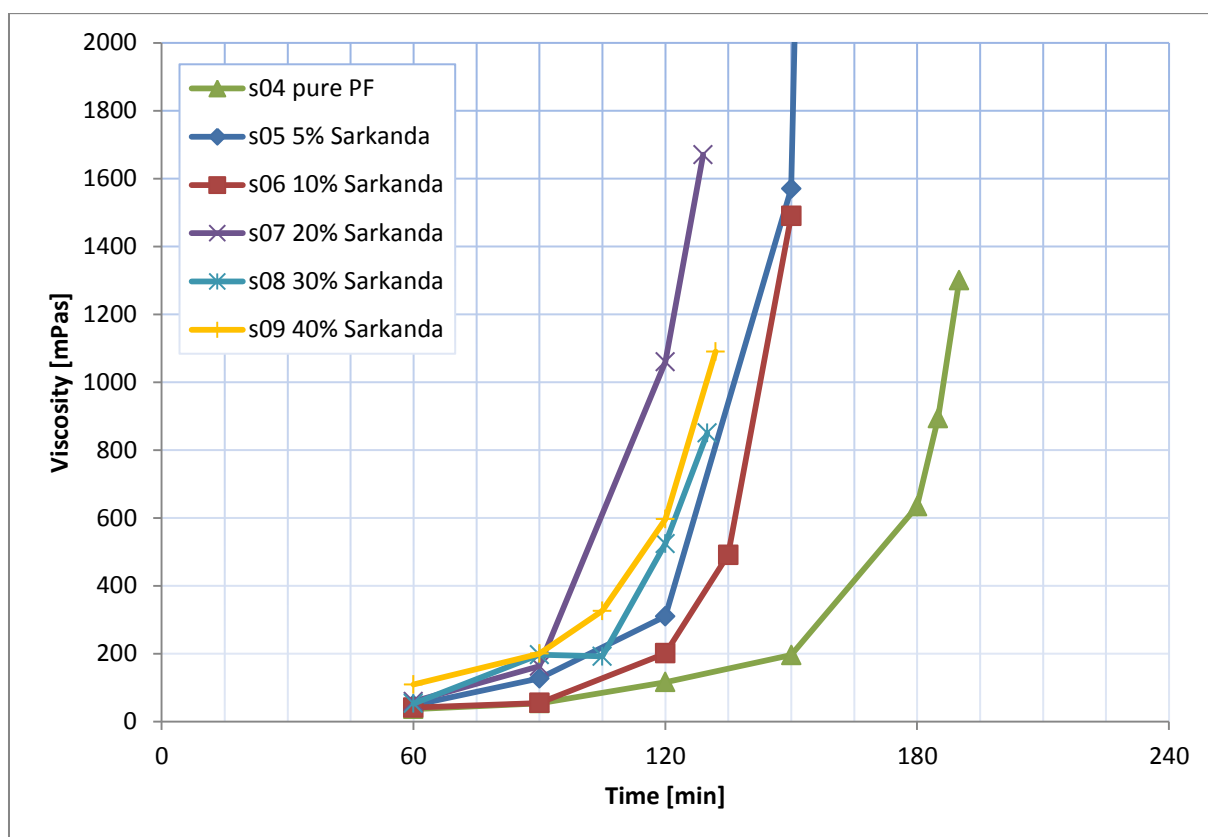


Figure 14: Results from the screening tests with 0-40% Sarkanda

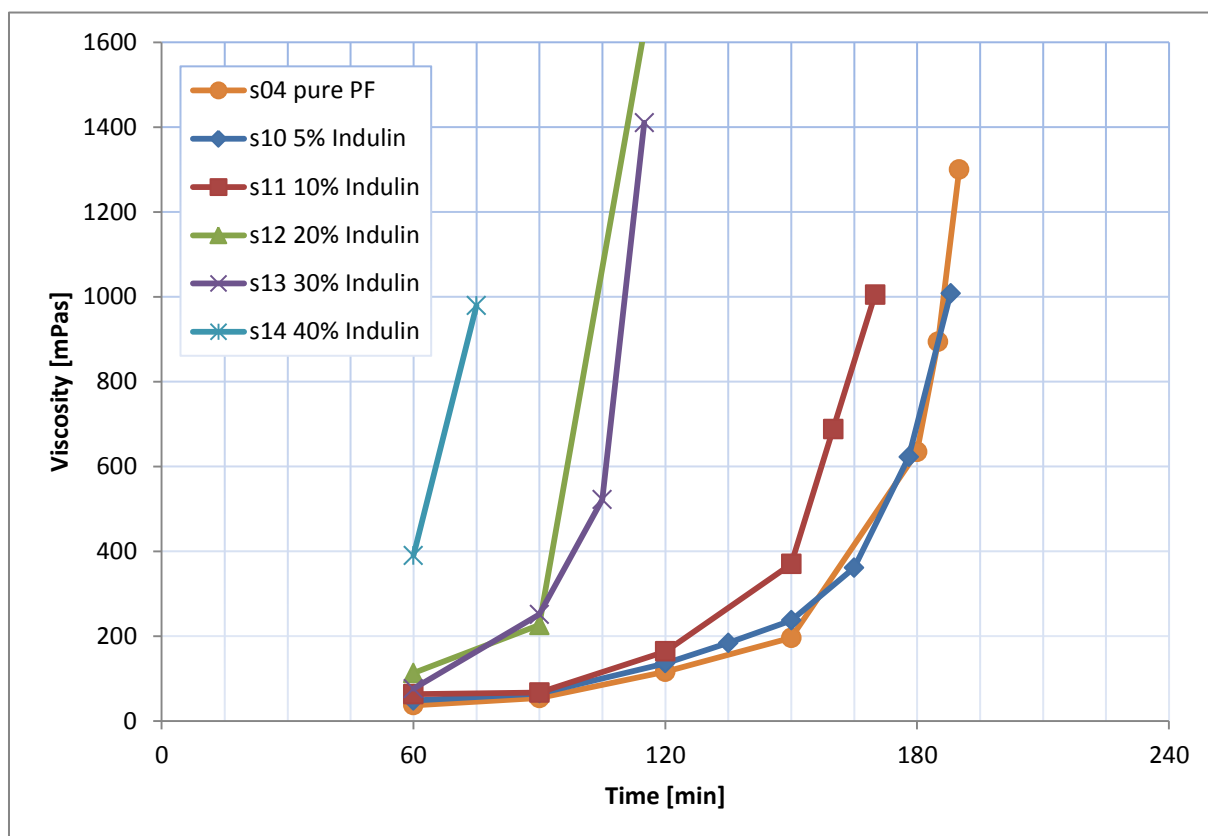


Figure 15: Results from the screening tests with 0-40% Indulin

Subsequently phenol was replaced by Indulin. In general viscosity was developing faster with an increasing substitution of phenol by Indulin as Figure 15 illustrates. Resin s10 with 5% Indulin shows no difference in the development of the viscosity compared to the pure PF resin.

At this point, the decision was made to continue with Sarkanda grass lignin for the whole thesis. The tests with Indulin were continued in another thesis, see STREIT (2014).

3.2 Reproducibility Test

The investigation was started with the test resins 01 (t01) to 05 (t05) with 20% Sarkanda. An overview of the procedure and the used equipment is listed up in Table 4. The target viscosity of approx. 1000mPas was reached after different times as Figure 16 illustrates.

In addition, the temperature progress of each resin was recorded every five minutes after the formalin addition was completed ($t=0$). Figure 17 shows the discrepancy between the target temperature and the effective temperature during the synthesis.

The addition of formalin started when the temperature of 65°C was reached inside the flask. After all formalin was added the temperature was set to 80°C and as Figure 17 displays, the temperature clearly exceeded the target temperature. Furthermore the temperature fluctuated during the whole synthesis which led to the next step.

To prevent temperature fluctuations during synthesis a contact thermometer ETS-D5 was purchased to control the temperature more accurately (Table 5). The temperature and viscosity trend over time for the resins t06 and t07 are shown in Figure 18. The graph shows that the temperature was increased smoothly but still had some peaks after some time. To be able to stop the curing at a certain point in the end, the target temperature was decreased from 80°C to 70°C, which is indicated with the red line in all following figures. The peaks in the temperature trend, as shown in Figure 17 and Figure 18, might be caused by the small amounts of resin. For the test a 250ml three neck round bottom flask was used for 37g of compounds. Due to the operating instructions at least 20mm of the contact thermometer's tip had to be inserted into the medium, in order to determine the temperature precisely. This requirement was not fulfilled under the conditions of 37g resins compounds in a 250ml flask. Hence, the sensor might have recorded the temperature with delay and controlled the heating unit with delay which led to a temperature overshoot. Therefore the scale for the following resins was increased to 8% of the basic calculation as mentioned before (Table 6), to assure that the sensor is inserted at least 20mm.

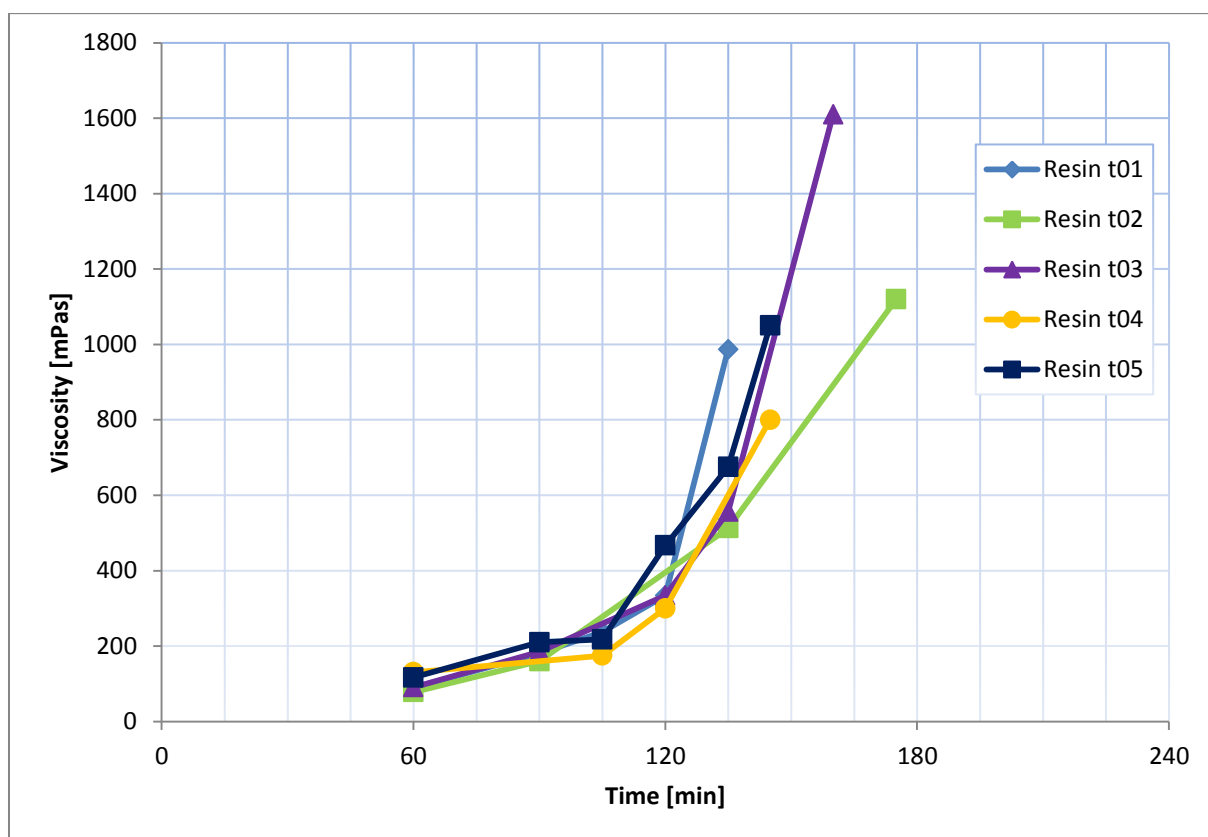


Figure 16: Viscosity trend over time for resins t01 - t05

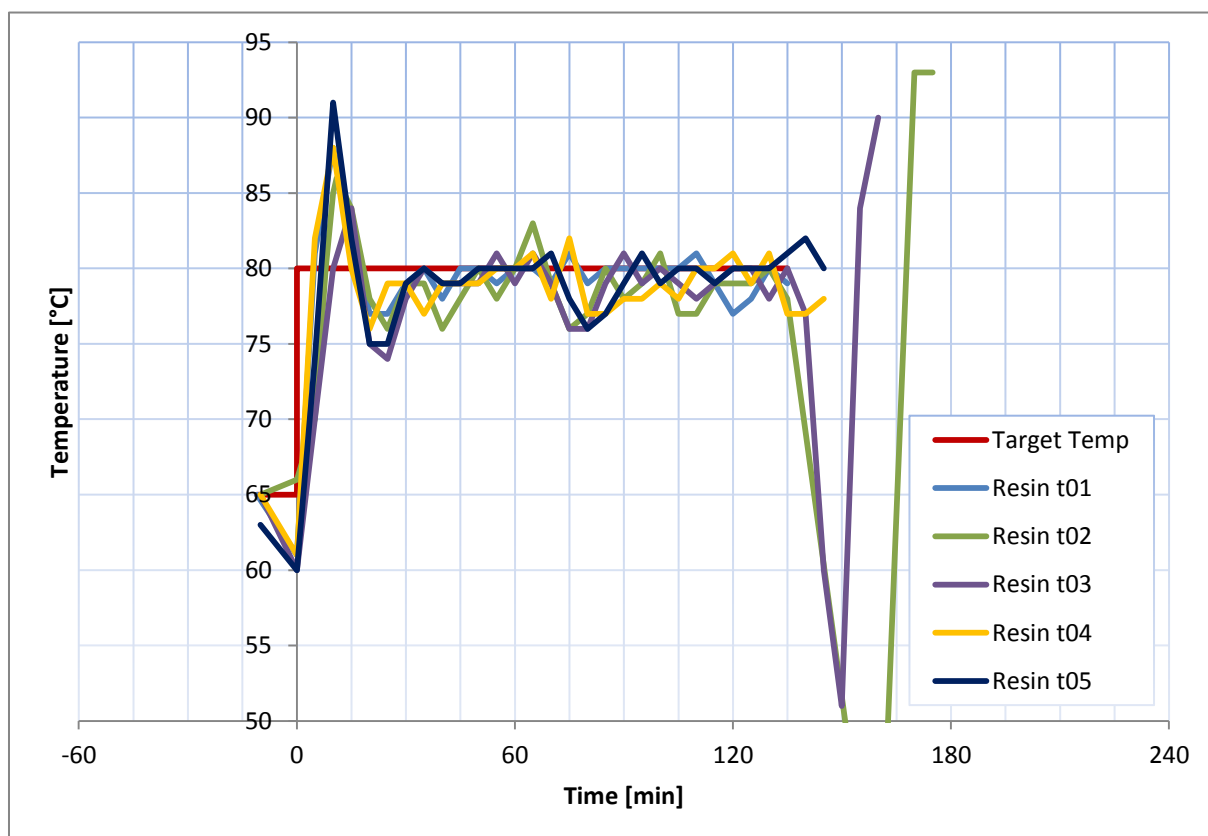


Figure 17: Temperature trend over time for resins t01 - t05

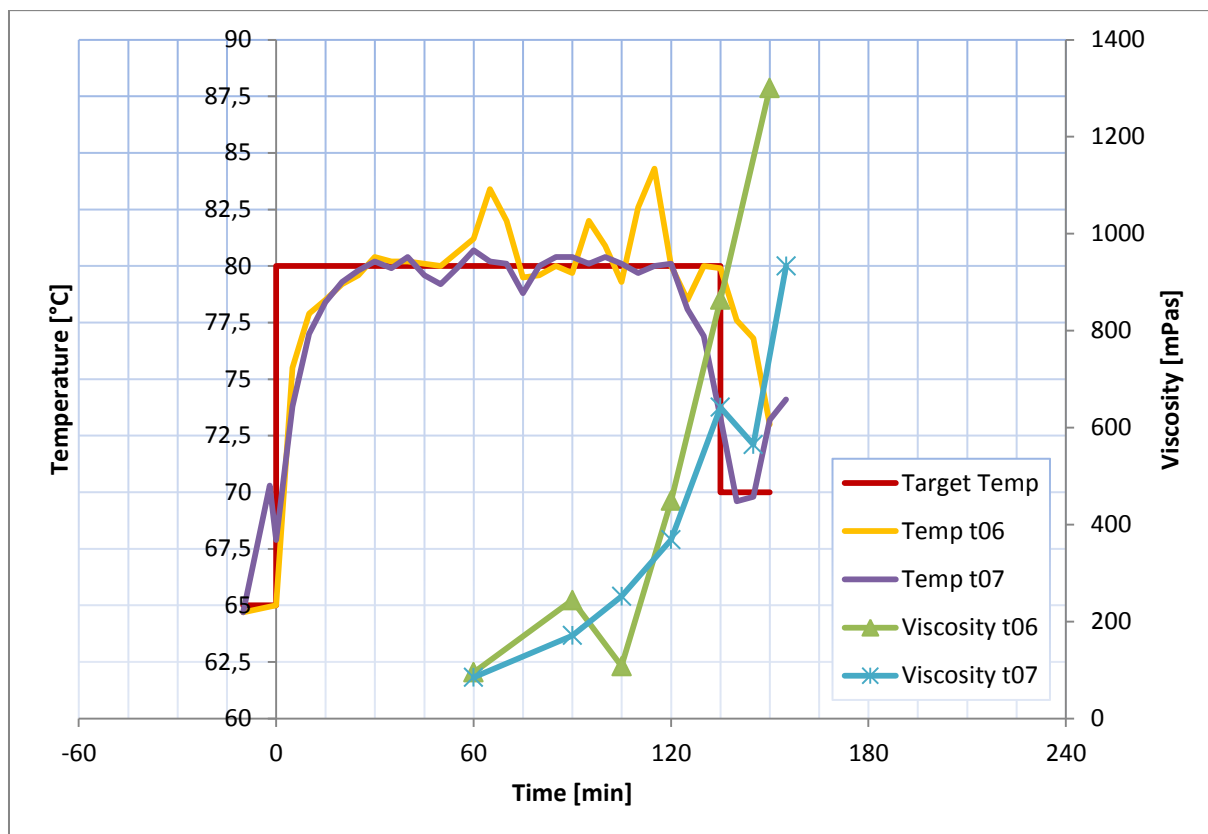


Figure 18: Temperature and viscosity trend over time for resins t06 - t07

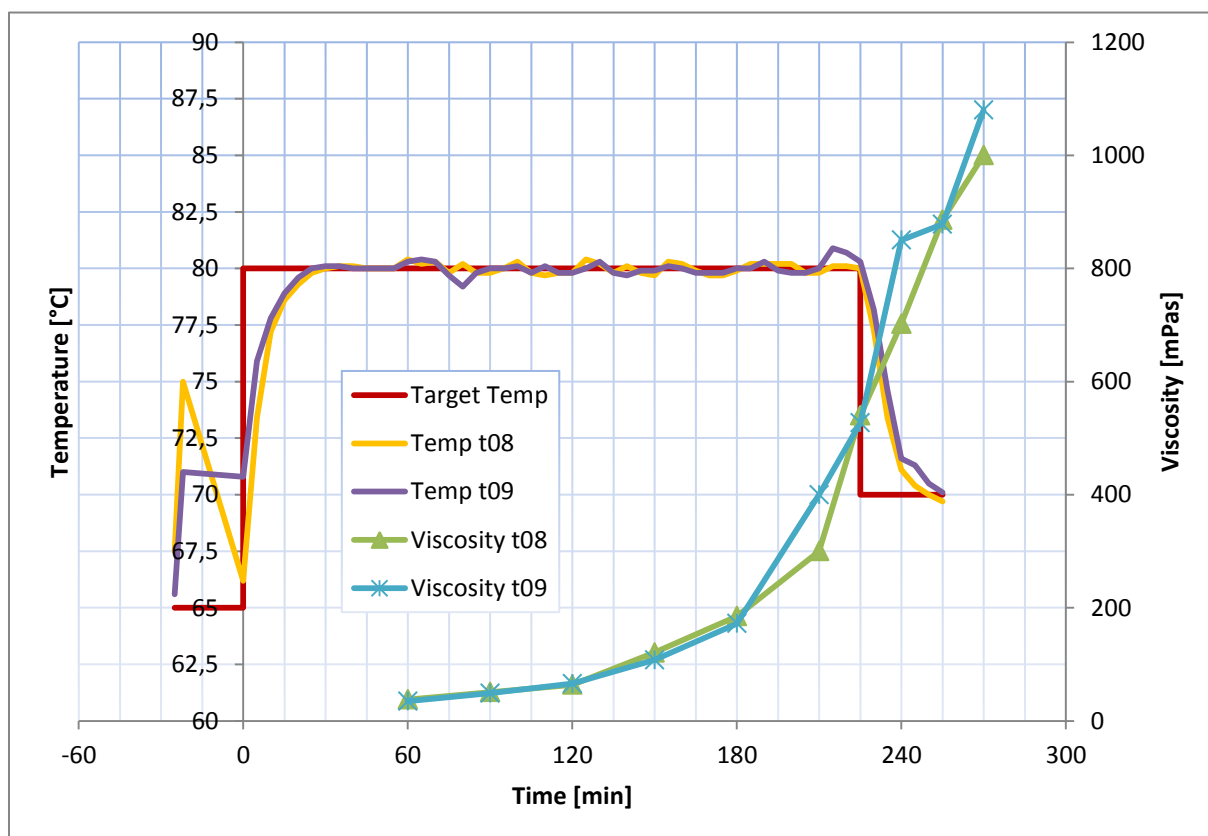


Figure 19: Temperature and viscosity trend over time for resins t08 - t09

Results show that the final viscosities lie in a very small range for the resins t08 and t09 after 210 minutes. Furthermore the comparison of the two resins shows very little deviations in the temperature trend. Just at the beginning there was a difference in the peak during the formalin addition (Figure 19). The use of the contact thermometer in combination with the increased scale shows a huge improvement. Therefore the changes have been maintained for the further synthesis development.

As the process showed low varieties at temperature and viscosity, Sarkanda lignin was added again for the next resins (Table 7). The results show that the variation of viscosity is higher than in the previews tests. The temperature trend was analysed and it was noticeable that the temperature during the formalin addition for each resin is different, as illustrated in Figure 20 for temperature and in Figure 21 for the viscosity. From the point on where all compounds were mixed together, the temperature fluctuations were quite low, whereas the viscosity still shows big differences. It was assumed that the different temperature peaks at the formalin addition are caused due to the non-constant volume flow of formalin which in further consequence effected the viscosity development. Hence, the dropping funnel was replaced by a peristaltic pump as described in chapter 2.4 Procedure.

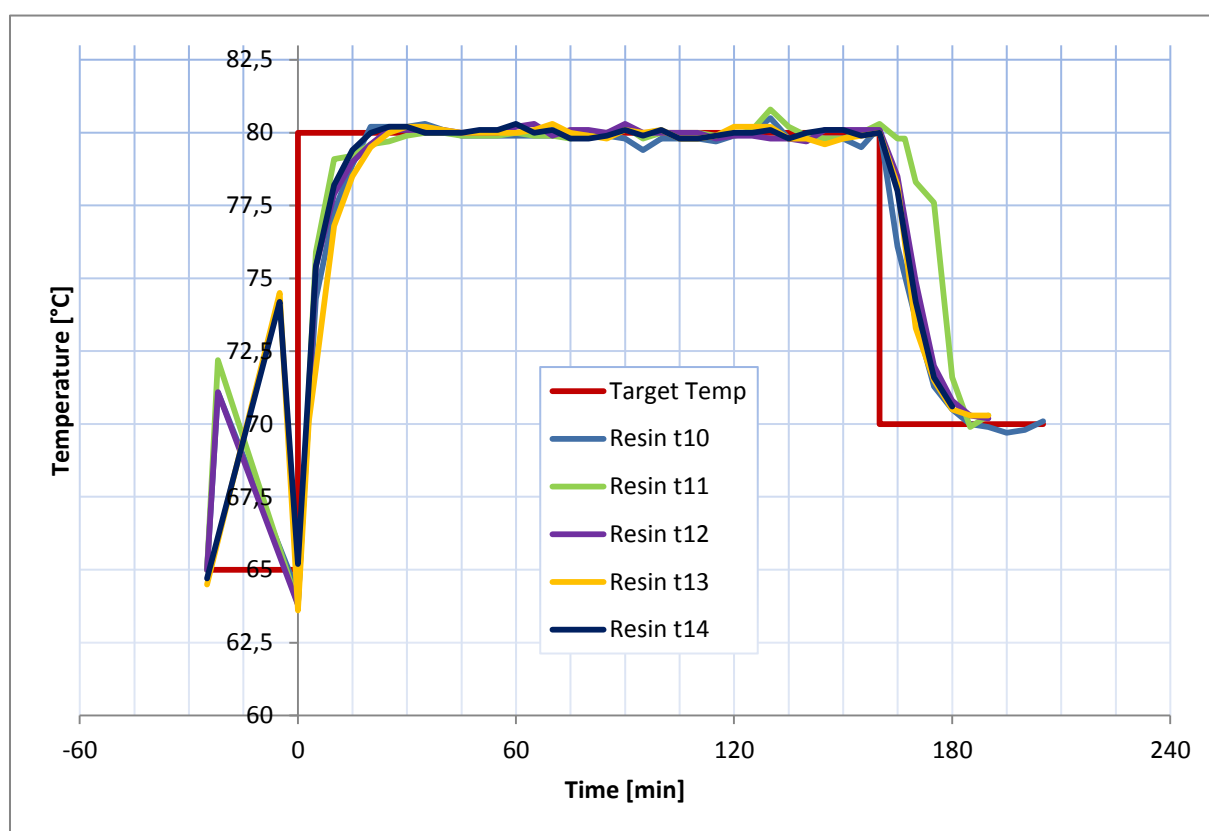


Figure 20: Temperature trend over time for the resins t10 - t14

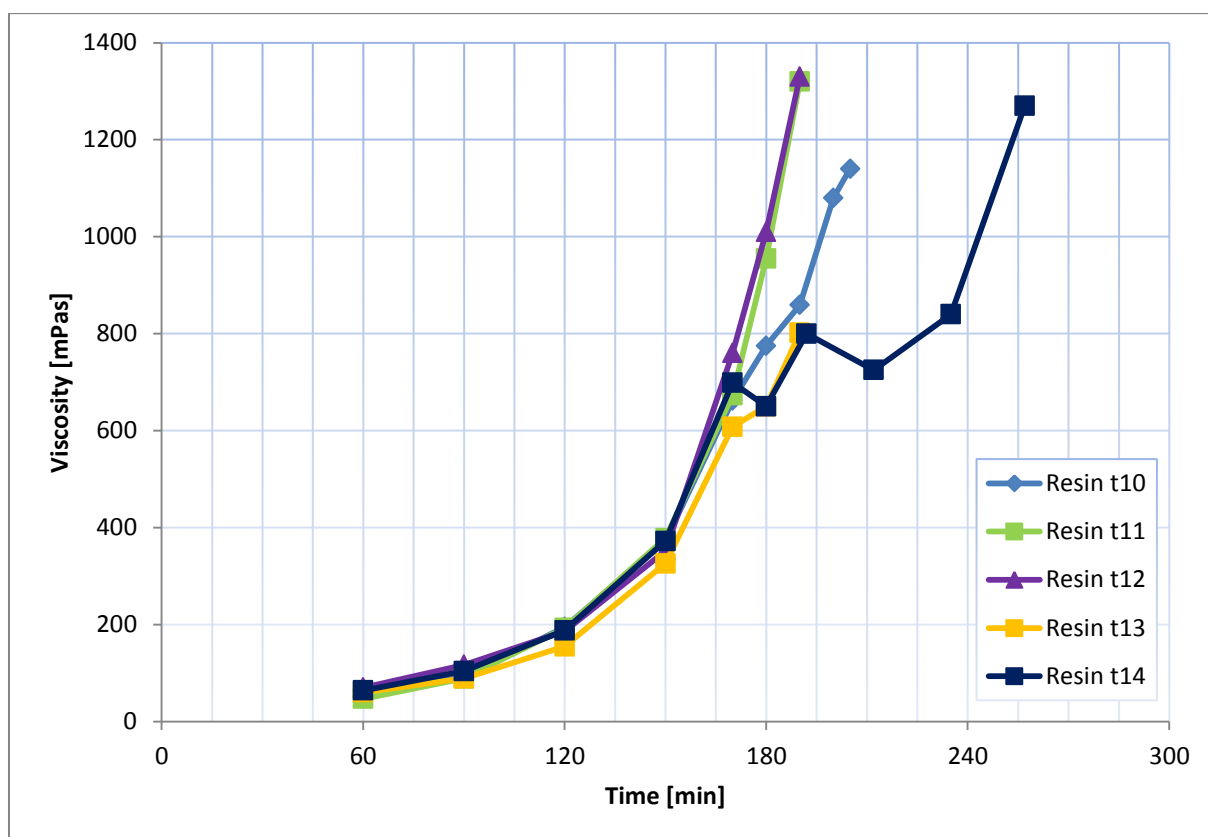


Figure 21: Viscosity trend over time for the resins t10 - t14

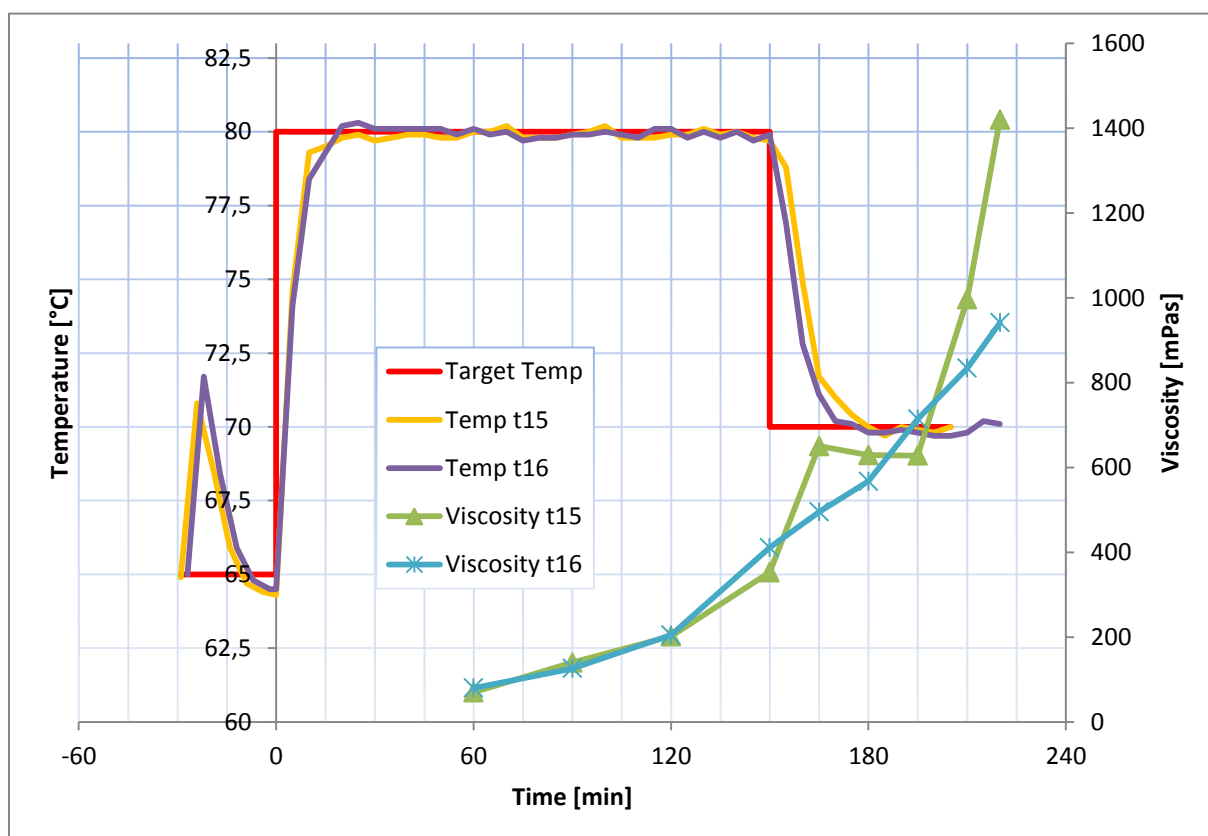


Figure 22: Temperature and viscosity trend over time for resins t15 - t16

Although the temperature fluctuations during formalin addition were reduced due to the peristaltic pump, huge deviations of the final resins viscosities were achieved (Figure 22). To improve the procedure again the peristaltic pump was replaced by a Titration device and the viscosity measurements were done with a rheometer with a temperature control unit (Table 9). To show the importance of constant temperature for the viscosity measurement, resin t15 was used to test the viscosity trend over the temperature. Due to the fact that viscosity is strongly influenced by temperature, it was tested if the procedure described in chapter 2.8.1 was sufficient. As mentioned above the portable thermometer had an accuracy of $\pm 2^\circ\text{C}$. The target temperature was 20°C (room temperature). That means that even if the thermometer showed 20°C the area of the real temperature level lay between 18 to 22°C and more likely on the upper area.

Figure 23 illustrates that only an increase of 5°C results in a dramatic decrease of viscosity. For the case described above this results lead to the fact that a huge area was explored before and that the values of viscosity are not exact. Additionally the temperature was not the same for all measurements within a resin. So the range where the real viscosity lies, is even bigger. For example describes NAIR (2004) also an enormous decrease of viscosity depending of the temperature for a novolac.

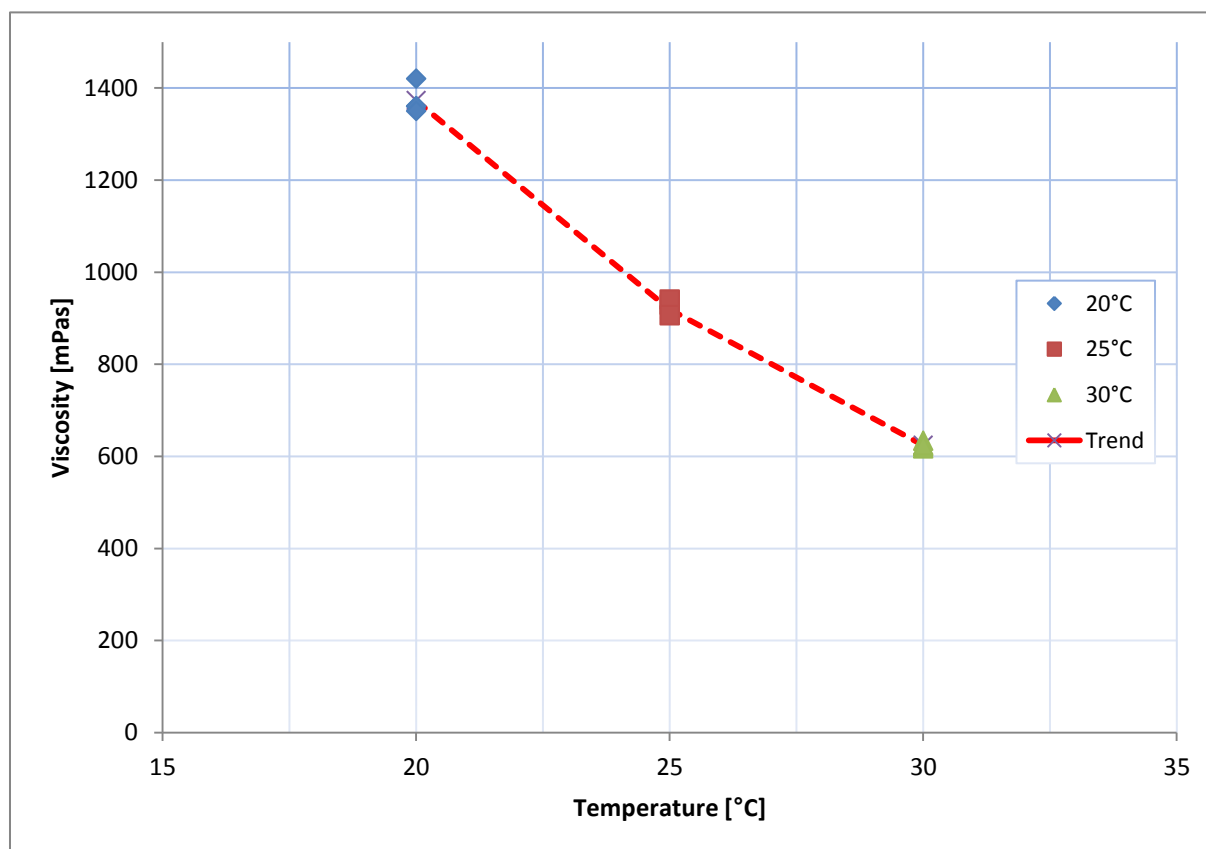


Figure 23: Effect of temperature on viscosity (resin t15)

The fluctuations in the viscosities for resins t01 to t07 as shown in Figure 16 and Figure 18 could be mainly caused by the use of the rheometer without temperature control unit.

After the observation of the big importance of the temperature at the viscosity determination, the runaways for Resins t06 and t07 (Figure 18) might be explained as a reduction in viscosity during synthesis is highly unlikely. It is more likely that the temperature at the viscosity measurement was increased compared to the previous measurements. Another source of error could be that the applied amounts were not the same between the points. With a big probability the most important factor is the temperature and the error caused by the different amounts of resin is negligible.

Resins t17 to t19 show low variabilities for the temperature and the viscosity trend. A slight deviation is noticed at the second last value of resin t17, apart from this the trend indicates to be constant (Figure 24).

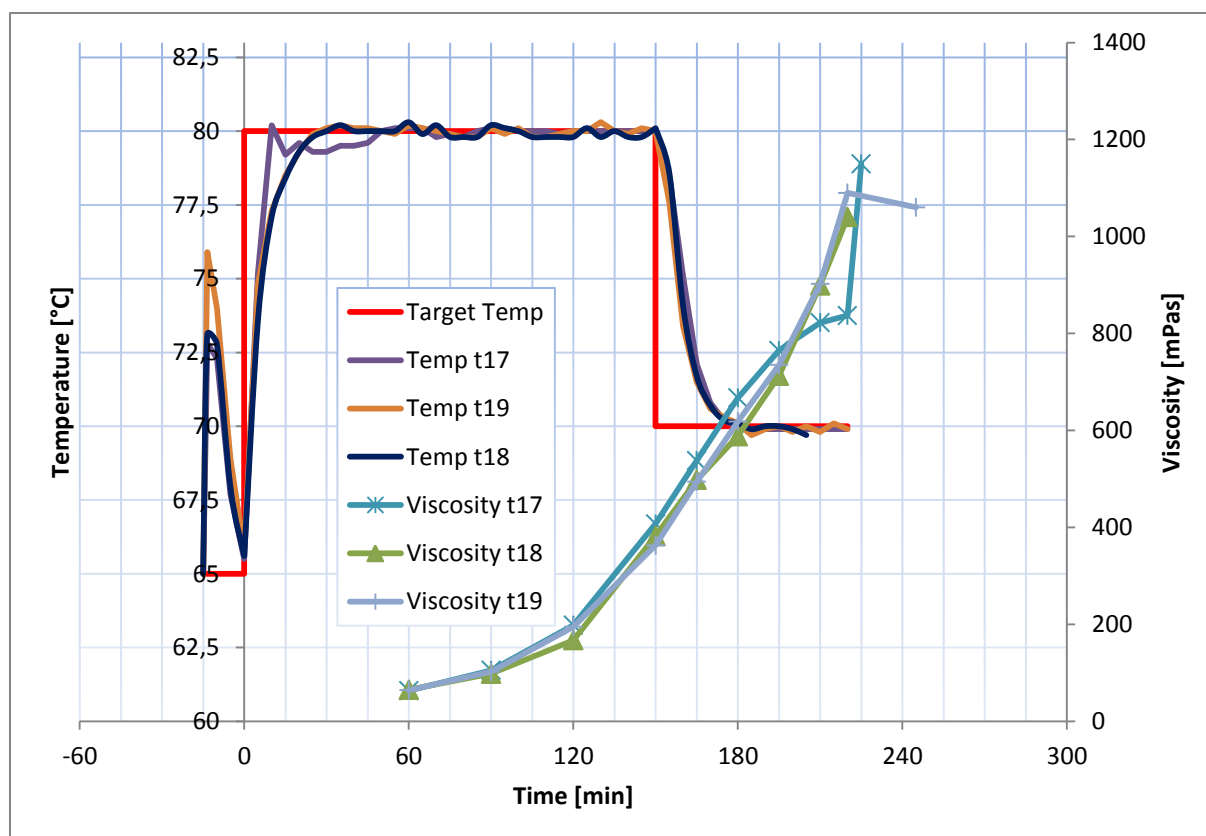


Figure 24: Temperature and viscosity trend over time for resins t17 - t19

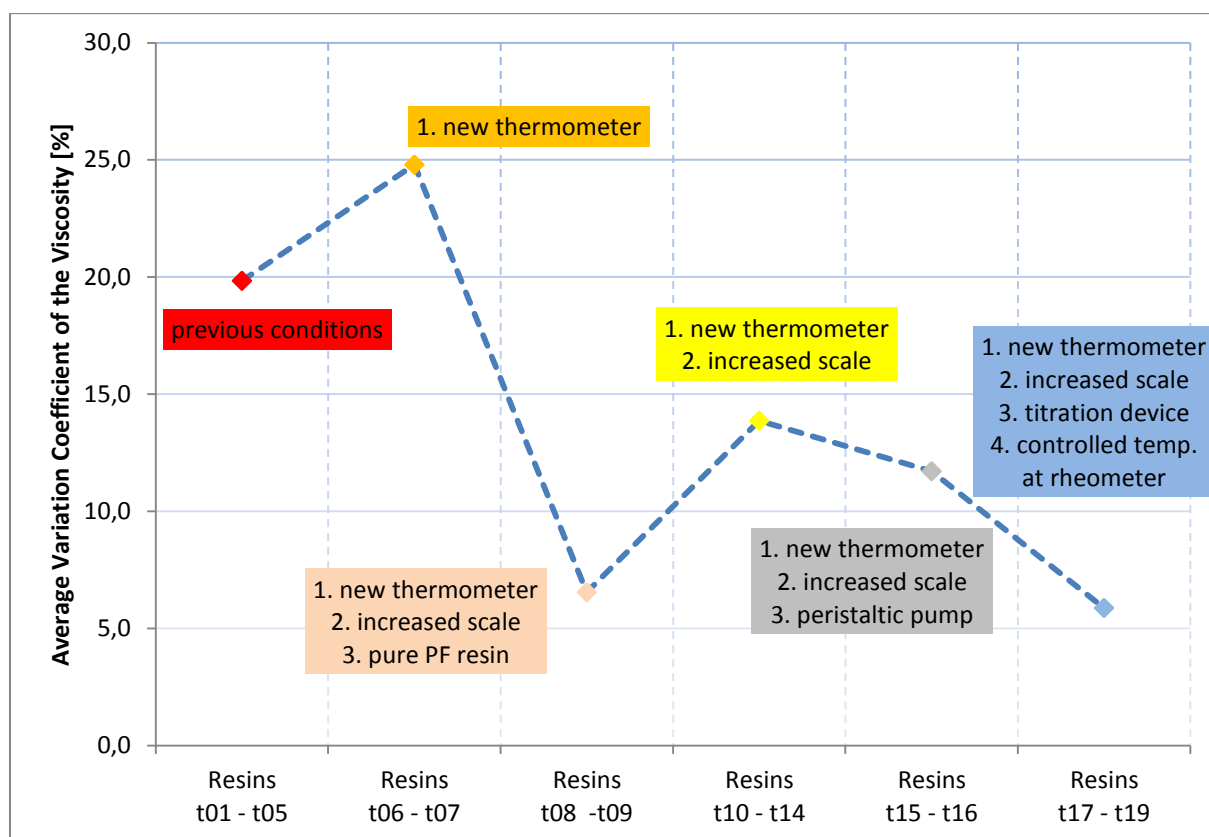


Figure 25: Average variation coefficient of the viscosity of each group for the reproducibility tests

Figure 25 shows a final comparison of the average variation coefficient of the viscosity of each group for the reproducibility tests. The viscosity was determined at the same time of production within a group to calculate the mean and the standard deviation at this point. To obtain a variation coefficient the standard deviation was divided by the mean. Finally the mean of these coefficients was calculated which led to the average variation coefficient of a group.

The slope of the dotted line implies an increase and reduction of the relative standard deviation. The main changes in the synthesis procedure are plotted as well. The first resins were produced with the initial procedure. The average variation coefficient for resins t01-t05 lay around 20%. With the new thermometer the deviations were increased instead of being reduced (t06 - t07), caused by an insufficient operated temperature sensor which has been described above in detail. The pure phenol formaldehyde resins t08 – t09 showed a average variation coefficient of 6.5%. For the next groups Sarkanda was added again, which led to an increased deviation of 13.9% (t10-t14). A slightly improved average variation coefficient was achieved with a peristaltic pump. An average variation coefficient of 5.9% was achieved with an additional titration device and a temperature controlled rheometer for resins t17-t19. A reduction of the average deviation coefficient of 20% to 6% at this point was considered to be acceptable and it was continued with the synthesis of the final

resins. The detailed results of the variation coefficients are listed up in Table 14 to Table 19 in the appendix.

For some resin groups just two adhesives were produced and the mean and the standard deviation calculated. In general three values are always necessary, but in case the trends of viscosity and temperature showed big fluctuations the test conditions were adapted as the procedure was not sufficient.

3.3 Characterization of Resins

The temperature trends and viscosity trends are shown in Figure 26 and Figure 27. In both figures it is clearly shown that the synthesis time decreased with an increased content of Sarkanda lignin. The observation in chapter 3.1 Screening Tests that viscosity increases fastest for resins with 20% Sarkanda could not be confirmed. In fact, the higher the amount of Sarkanda lignin, the faster is the development of the viscosity. It is assumed that the increase of viscosity is related to an increased molecular mass (PECINA et al., 1994) which is an explanation for the faster viscosity development of the adhesives. Compared to phenol Sarkanda lignin has a higher molecular mass of about 1000-2000g/mol (ASIKKALA et al., 2012), which leads in further consequence sooner to a higher viscosity.

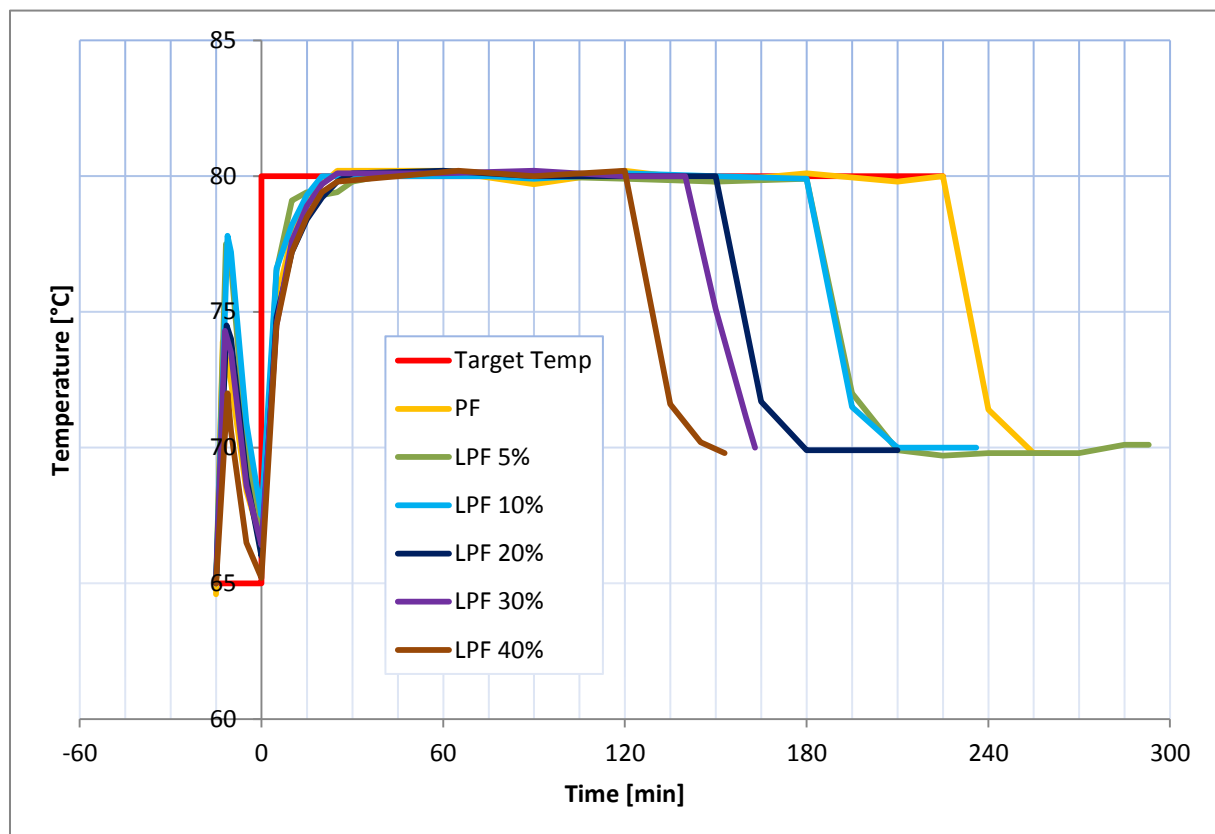


Figure 26: Temperature trend over time for final resins

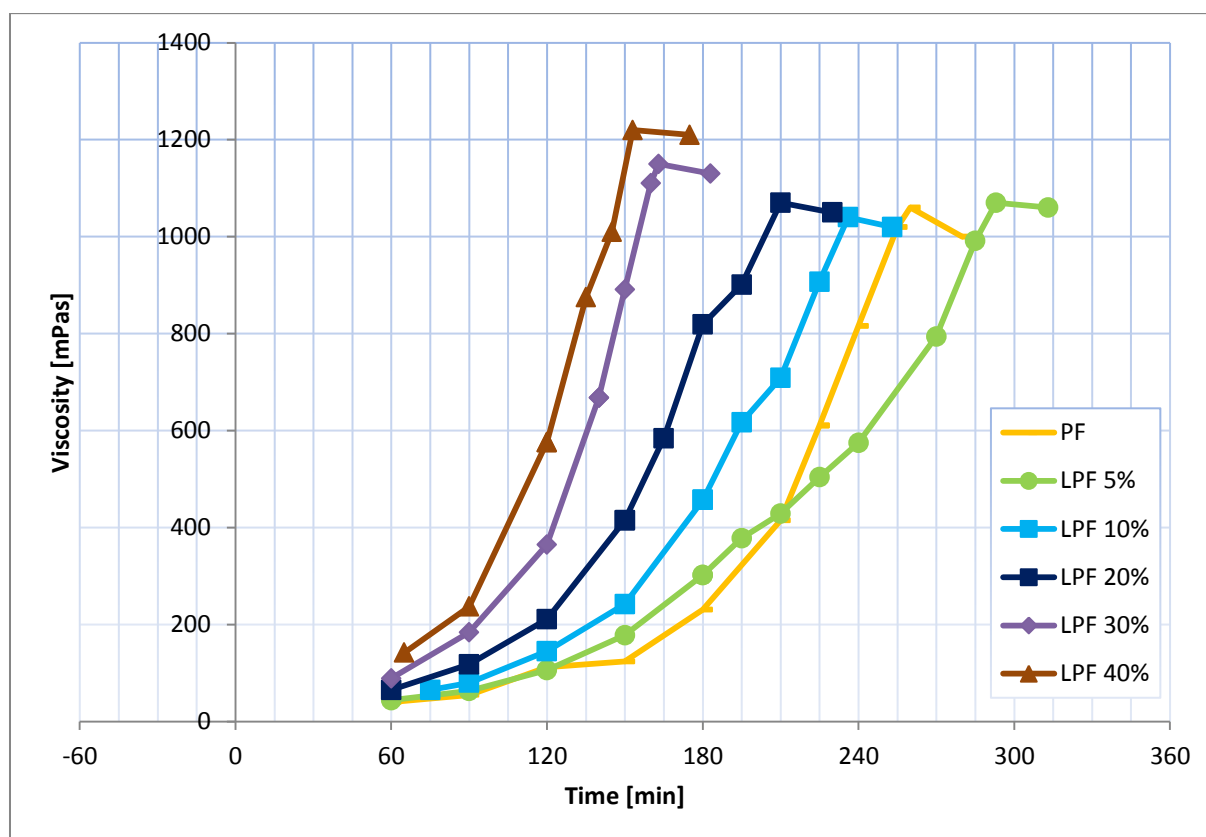


Figure 27: Viscosity trend over time for final resins

The ultimate viscosity, the pH, the B-time at 100°C and 130°C, water miscibility and solid content of the adhesives are listed up in Table 10. The pH stayed for all resins the same as well as water miscibility. A slight reduction of the solid content was observed for 20, 30 and 40% substitution of phenol. Big deviations show the B-time at 100°C where the B-time is increasing from adhesives with 5 to 40% Sarkanda. The B-Time at 130°C drops from 2 minutes for the reference resin to approx. 96 seconds for all other resins except LPF 40%. B-Time of the latter is again increased. As a criticism of the determination of the B-Time it can be noted that the temperature sensor was in a distance to the surface of the B-Time plate. By doing so the exact temperature on the surface could not be determined accurately. This also might effect the pressing time since it is based on the B-time at 100°C. Although a safety factor of 2 was applied the curing time of the resin during pressing might have been insufficient which leads to lower strength. ÇETIN and ÖZMEN (2002) refer a solid content for lignin phenol formaldehyde resins with 5 to 40% substitution of 50 to 55%. The pH in this work is 10.2. The viscosity of these resins laid between 200 and 250mPas at 25°C, which is not comparable to the results in Table 10. It also has to be mentioned that the resins in the work of ÇETIN and ÖZMEN were used for particleboard production whereas the herein used adhesives were used for massiv wood. For the various applications of an adhesive special viscosities are required as mention in chapter 1.3.

Table 10: Summary of the determined characteristics of the resins

Declaration	Viscosity at 20°C	pH		B-Time 100°C	B-Time 130°C	Water Miscibility	Solid Content
[1]	[mPas]	[1]	at [°C]	[min:s]	[min:s]	[ml]	[%]
PF	1000	10.89	23.8	08:35	02:01	infinite	46.45
LPF 5%	1060	10.78	24.4	06:40	01:39	infinite	46.46
LPF 10%	1020	10.55	23.9	06:55	01:37	infinite	46.36
LPF 20%	1050	10.56	21.7	07:20	01:36	infinite	45.27
LPF 30%	1130	10.70	23.1	07:16	01:37	infinite	43.82
LPF 40%	1210	10.33	23.4	10:28	02:20	infinite	42.89

The viscosity and the pH are the values after the synthesis, the shown B-Times are an average value of two measurements

Table 11: Change in water miscibility of the resins over time

Declaration	Date of Production	Water Miscibility	Date of Testing	Storage Time	Water Miscibility
[1]	[1]	[ml]	[1]	[days]	[ml]
PF	26.03.2014	infinite	29.04.2014	34	NA*
LPF 5%	31.03.2014	infinite	29.04.2014	29	infinite
LPF 10%	02.04.2014	infinite	29.04.2014	27	infinite
LPF 20%	19.03.2014	infinite	29.04.2014	41	infinite
LPF 30%	07.04.2014	infinite	29.04.2014	22	infinite
LPF 40%	09.04.2014	infinite	29.04.2014	20	infinite

* this value could not be determined, due to the fact that not enough resin was left for the test

To see if the properties are changing during time, the test for water miscibility and the viscosity were repeated after a certain time of storage. No change in water miscibility was observed after storage in a fridge for at least 20 days (Table 11). Table 12 shows that the viscosity increased over the time. For each resin the viscosity increased unequally. The lowest increase can be observed for resins with 20% Sarkanda (LPF 20%).

Table 12: Change in viscosity of the resins over time

Declaration	Date of Production	Viscosity at 20°C	Date of Testing	Storage Time	Viscosity	Change per Day
[1]	[1]	[mPas]	[1]	[days]	[mPas]	[mPas]
PF	26.03.2014	1000	29.04.2014	34	1490	14
LPF 5%	31.03.2014	1060	29.04.2014	29	1330	9
LPF 10%	02.04.2014	1020	29.04.2014	27	1520	19
LPF 20%	19.03.2014	1050	29.04.2014	41	1270	5
LPF 30%	07.04.2014	1130	29.04.2014	22	1580	20
LPF 40%	09.04.2014	1210	29.04.2014	20	1550	17

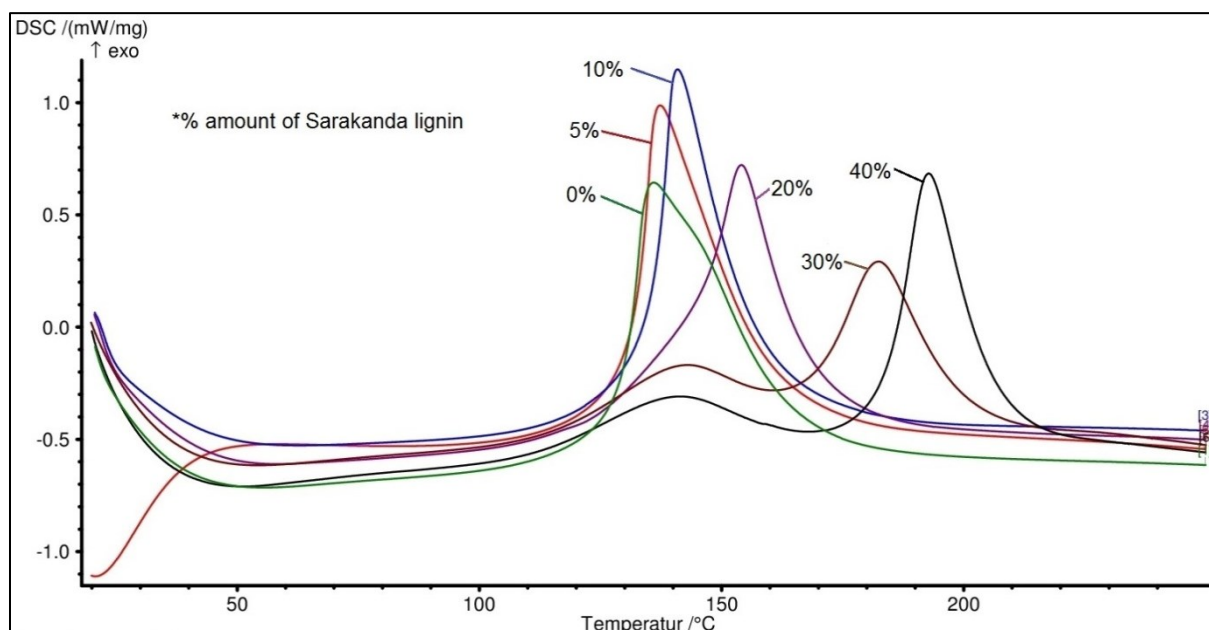


Figure 28: Comparison of DSC results of the resin groups

The evaluation of the differential scanning calorimetry in Figure 28 shows the exothermic curves of each resin which indicates that higher amounts of phenol substitution by Sarkanda lignin are shifting the exothermal peaks to the right, meaning that the curing reaction takes place later. Two peaks are occurring for LPF 30% Sark and LPF 40% Sark.

As referred in CHRISTIANSEN and GOLLOB (1985) the lower peak is caused by methylation and the upper peak is caused by condensation reaction. The shifts of the curves are indicating that methylation take place in the curing process before the final hardening to a three dimensional structure occurs. It gets stronger for resins with 20% Sarkanda (LPF 20%) and finally leads to a peak of methylation and to a separate peak of condensation for resins with 30 and 40% Sarkanda as described above. The polycondensation reaction leads to oligomers and further on to a three dimensional network. The conclusion is that the time for methylation was inefficient. After all compounds were mixed together and the temperature of 65°C was reached, the temperature was immediately raised to 80°C to initiate the building process of oligomers regardless the added amount of lignin.

Figure 28 displays a qualitative change of the behavior of the resins. The results of the adhesives with different phenol substitution percentage are presented in Table 13. It clearly can be seen that the reactions start at higher temperatures (Onset) even if there are two peaks which lead to the higher peak temperatures. WANG et al. (2009) report the same effect of curing behavior for increasing lignin content for Organosolv pine lignin. It is also reported that the onset, peak and offset of adhesives with less or equal than 40% phenol substitution is lower compared to pure phenol-

formaldehyde resins. Thus the thermal cure is lower for these resins. Sarkanda lignin in this work had the opposite effect in the range of 5-40% phenol substitution on the thermal cure of a resin. Peak 1 was for all binders with lignin higher but the range between offset 1 and onset 1 for the resins LPF 5%, LPF 10% and LPF 20% was smaller.

Table 13: Cure temperatures of the resins at a heating rate of 10K/min

		Onset1	Offset1	Offset1- Onset1	Peak1	Onset2	Offset2	Offset1- Onset1	Peak2
		[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]
LPF 0%	Mean	129.0	164.7	35.7	135.9	-	-	-	-
	Std. deviation	0.3	0.7	1.0	0.2	-	-	-	-
LPF 5%	Mean	131.4	162.0	30.6	137.7	-	-	-	-
	Std. deviation	0.2	0.4	0.4	0.3	-	-	-	-
LPF 10%	Mean	134.6	158.1	23.5	140.9	-	-	-	-
	Std. deviation	0.1	0.8	0.7	0.0	-	-	-	-
LPF 20%	Mean	140.3	167.8	27.6	153.0	-	-	-	-
	Std. deviation	0.7	1.1	0.4	1.0	-	-	-	-
LPF 30%	Mean	114.7	155.7	41.1	142.6	170.4	198.0	27.6	182.2
	Std. deviation	1.6	1.0	0.9	0.4	0.1	0.9	0.8	0.3
LPF 40%	Mean	113.4	161.2	47.8	141.9	184.2	207.1	22.9	193.2
	Std. deviation	1.3	1.6	0.7	0.9	0.7	1.1	0.4	0.8

Mean and standard deviation were calculated from three DSC measurements

The curing temperature is increased with increased amount of Sarkanda as Peak 1 indicates for 0 to 20% Sarkanda. The onset is also increased which means that the reaction starts later. For the resins with 30 and 40% lignin the first peaks are the same, the second peaks differ from each other. For LPF 40% it starts later and the peak reached a higher temperature (Table 13). Other values for peak temperature for pure phenol resins lie between 98 and 129°C for the lower peaks and between 139 - 151°C for the upper peaks (CHRISTIANSEN and GOLLOB, 1985). Compared with the results of the literature these results are increased. A reason might be the different chemical composition of the resin and a different synthesis procedure. Figure 29 shows the linear correlation of free formaldehyde to the used amounts of Sarkanda lignin in the resins. The coefficient of determination is 0.9996 which indicates that the estimated average free formaldehyde content can be described by the amount of Sarkanda lignin used for the adhesive. The fact that methylation occurs at a later time is also an indicator for the trend of the free formaldehyde content. CHRISTIANSEN and GOLLOB (1985) report that the intensity of the first peak increases with free formaldehyde content. Although just phenol formaldehyde resins without lignin were evaluated, the conclusion can be drawn that the correlation is also valid for adhesives with lignin. It is also referred that one reason of the delayed reaction may be the lower reactivity or lower accessibility of the reactive positions of the phenolic rings in lignin. A second reason might be that formaldehyde converts to a polymeric structure as the concentration increases which leads to a

lower availability. ÇETIN and ÖZMEN (2002) synthesized lignin phenol formaldehyde resins with 5, 10, 20, 30 and 40% phenol substitution with lignin. The free formaldehyde for rising lignin contents were 2.4 , 3.4 , 3.87 , 5.21 and 5.76%. The commercial reference resin for particle boards had a free formaldehyde content of 0.2%. The lower values for free formaldehyde might be the result of the longer synthesis at lower temperatures (1h at 50°C) where formaldehyde has more time to react with the phenolic compounds.

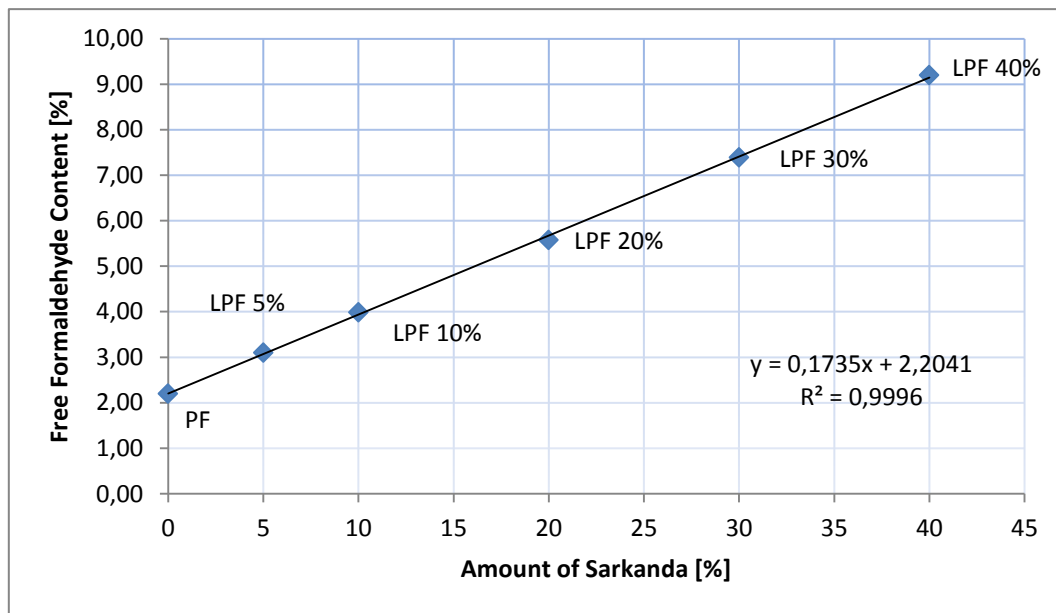


Figure 29: Free formaldehyde content of the resins
Illustrated with the mean of each group, sample size of the groups = 3
(GHORBANI, 2014)

3.4 Lap Shear Test

The test was performed according to ÖNORM EN 302-1 (2004) and the evaluation was conducted according to ÖNORM EN 301 (1992). The mean density over all used boards for gluing was 0.645 g/cm³ with a standard deviation of 0.031 g/cm³. The mean for the moisture according to the electrical resistance method was 11.7% with a standard deviation of 0.4%. The oven method-dry had showed a mean of 11.3% with a standard deviation of 1%. The standard claims a density of 0.7 ± 0.05g/cm³ and a moisture of 12 ± 1% of each board. Half of the used boards did not fulfill the density requirements. According the determination with the moisture meter the moisture requirements were fulfilled. The moisture was undercut by 13 out of 36 boards according to the oven-dry method.

Figure 30 shows the results of the lap shear test for each adhesive group and treatment plotted as a boxplot. No outliers are displayed in Figure 30 wherefore the whiskers show the maximum and minimum value of a group. The resin groups PF

and LPF 5% of treatment A1+ according the standard (standard climate) shows the highest values for this category, whereas at treatment A2 according to the standard (water storage) group LPF 40% shows the highest result and also the biggest variation. All detailed values are listed up in Table 20 and Table 21 in the appendix. The average shear strength for the groups PF and LPF 5% is above 10N/mm² and for the rest of the groups of category standard climate the average is between 8 and 9N/mm². For water storage the average lies between 3.2 and 5N/mm² which was achieved by the group LPF 5% respectively by the group LPF 20%.

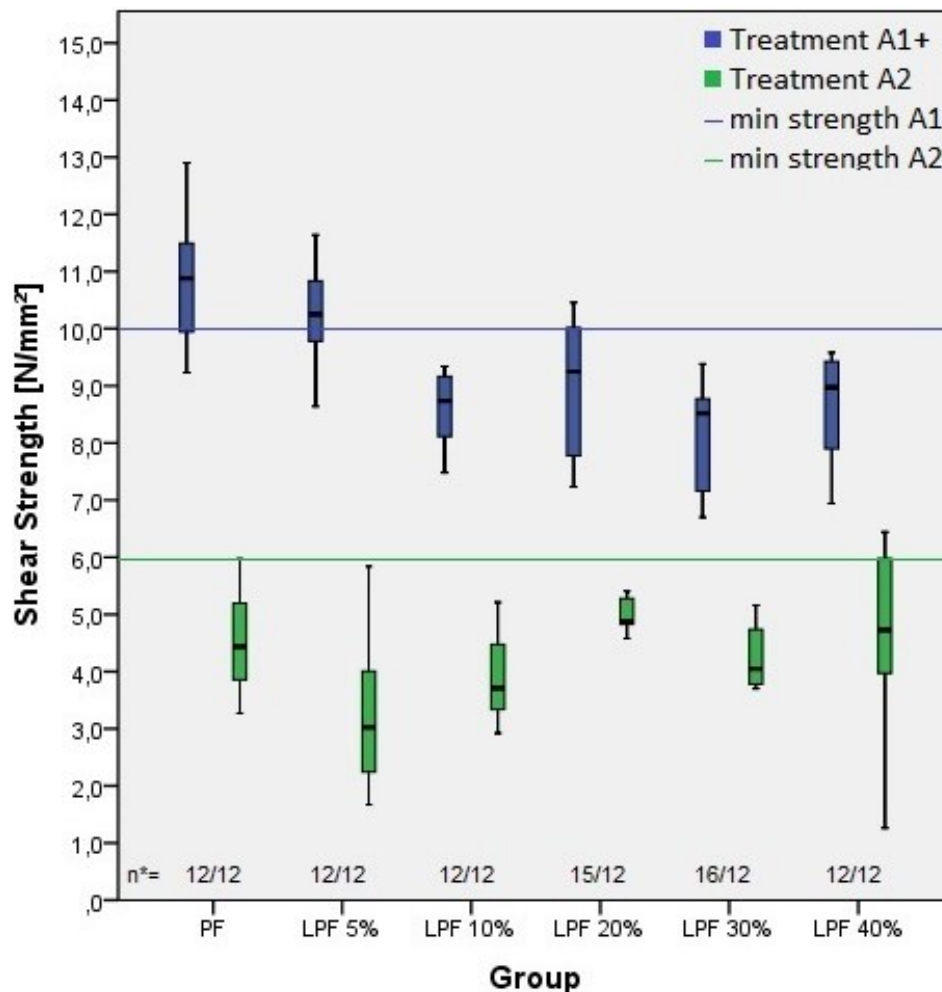


Figure 30: Shear strength of the adhesive groups

* n = number samples tested

Different other adhesives like Casein, PVAc, MUF, PRF and PUR achieve in dry conditions with beech wood an average shear strength of 10 N/mm² (KONNERTH et al., 2006). Although all groups showed almost 100% wood failure including some outliers at treatment A1+ (Figure 31) the average lap shear strength of the groups differ. No huge density fluctuations or fiber deviations were observed. Nevertheless did 50% of the boards not fulfill the density requirements. This might be a reason for the lower shear strength at high wood failure.

As expected for category water storage (A2) the average values of the groups are lower than for standard climate (A1+). The wood failure varied greatly in size as Figure 31 shows. It has to be noted that it was not easy to determine if it was a matter of wood or adhesive failure. Some samples indicate a surface like a sealskin where some wood and fiber parts were attached.

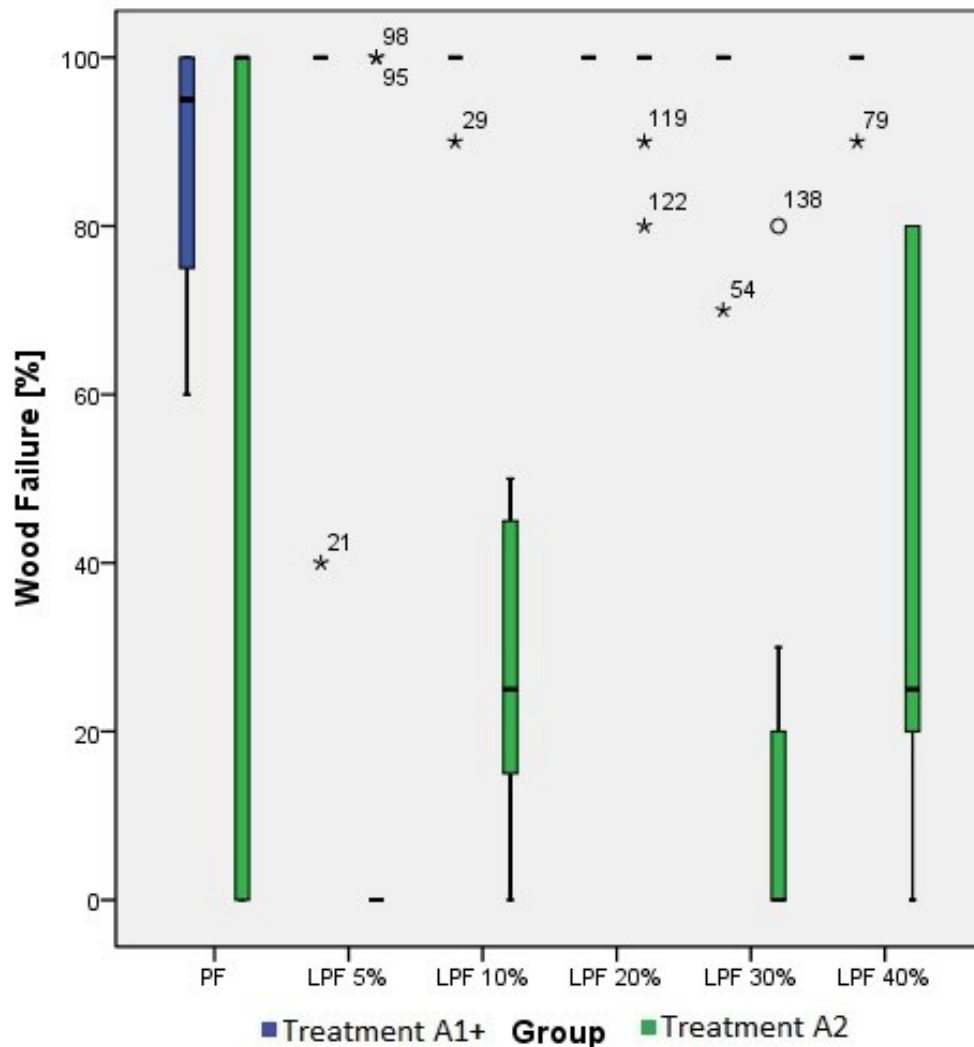


Figure 31: Wood failure of the adhesive groups

* outliers, left columns are treatment A1+ and right columns are treatment A2

The horizontal lines in Figure 30 mark the minimum shear strength for the two treatments beech specimens have to fulfill in order to reach the performance requirements which are listed up in ÖNORM EN 301 (1992). Due to the fact that in other chapters of the standard like fiber damage explicit the average of internal bonding has to fulfill a certain level, it is interpreted that every lap shear sample has to fulfill the minimum requirements. As the boxplot in Figure 30 illustrates all minimum values of the groups are lower than the min. shear strength which are indicated by the horizontal lines. This clearly shows that no adhesive group has fulfilled the performance requirements for load-bearing timber structures. Boards with higher

densities and a higher adhesive spread rate for the gluing might increase the strength values. As mentioned in chapter 3.3 at the discussion of the B-Time the pressing time might be also a factor which should be evaluated.

Before the groups were tested with an ANOVA, the restrictions like normal distribution of the data, homogeneity of variance and independent values were checked. The variables for these two categories are independent. The Shapiro-Wilk test showed with a significance level of 5% that all groups of treatment A1+ are normally distributed except group LPF 30% ($p=0.038$). Due to the fact that the ANOVA is a robust test this can be ignored. The groups of water storage are all normally distributed (sig. level 5%). With a significance level of 5% the homogeneity of variances for the category standard climate can be accepted ($p=0.169$), whereas the hypothesis of homogeneity of variance for water storage has to be rejected ($p=0.004$). With the one way ANOVA it was tested if the average lap shear strength of the adhesive groups, of a treatment, is equal with a significance level of 5% (H_0). The alternative hypothesis is that at least one group mean is different within treatment (H_1).

The ANOVA for treatment A1+ (standard climate) shows that the null hypothesis (H_0) has to be rejected ($p=0.000$) and the alternative hypothesis (H_1) has to be concluded. The following post hoc test, after Scheffé (chapter 8.3.1, Table 25) shows that the groups PF and LPF 5% can be clustered to a subgroup and the other groups build another subgroup. Why the second subgroup has slightly lower values cannot be explained in a satisfactory way though might be caused by the low density and the adhesive spread rate which was set at the lower bound. Almost all samples of these category had 100% wood failure. Due to the fact that the density showed low variation the shear strength should be at one level.

For the ANOVA of treatment A2 (water storage) the null hypothesis (H_0) has to be rejected ($p=0.000$) and the alternative hypothesis (H_1) has to be concluded. The post hoc test after Tamhane (chapter 8.3.2, Table 29) which is applied in case that the homogeneity of variance is not fulfilled, shows, that the average lap shear strength of the group LPF 20% is bigger than for the groups LPF 5%, LPF 10% and LPF 30% (sig. level 5%). The comparison of the other groups with each other showed no significant difference in the average lap shear strength. As noted above the adhesive spread rate of 200g/m² was set to the downward limit. A higher spread rate might lead to higher shear strength especially at treatment A2 where the determination of the wood failure was not obvious.

4. Conclusion

With the performed screening and reproducibility tests it was possible to develop a proper and reproducible synthesis procedure. The produced adhesives showed comparable properties in terms of end viscosity (1000-1210mPas), pH (~10.5), water miscibility (all infinite) and B-time (1:37-2:20 min). An increased amount of lignin leads in general to an increased viscosity development during adhesive synthesis and to a higher free formaldehyde content. Results of the DSC show that an increased amount of Sarkanda lignin leads to a delayed curing process. This is indicated by the shifted exothermal peak and later on by the appearance of two exothermal peaks. The first one indicates that the time for methylation in the synthesis flask was too short wherefore this part has to be caught up later on and delays the condensation to oligomers and in further consequence to a three dimension structure. The results of the lap shear test show that no group either treatment A1+ or A2 fulfilled the minimum shear strength for load-bearing timber structures. It can be seen clearly that the groups with the reference resin and the resin with 5% Sarkanda performed better than the rest of the lap shear groups at treatment A1+ (standard climate). For treatment A2 (water storage) the results show a higher average lap shear strength of the groups with 0, 20 and 40% Sakanda compared to the other groups. The determination of the wood failure was not explicit.

There is still potential for improvement by optimizing the procedure in terms of the free formaldehyde content. To decrease the free formaldehyde content a longer retention time at the temperature level of 65°C is proposed to assure an optimal hydroxymethylation under these conditions. As mentioned above the process of the B-Time determination has to be evaluated again to assure a constant temperature at the surface of the B-Time plate. For the lap shear samples a higher adhesive spread rate of more than 200g/m² should be tested to evaluate the influence on the shear strength and to determine an efficient amount of resin for application.

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8. Appendix

8.1 Summary of Viscosity Development for the Test Resins

Table 14: Summary of viscosities of resins t01-t05

Resins t01 - t05								
Time	Viscosity t01	Viscosity t02	Viscosity t03	Viscosity t04	Viscosity t05	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	90	78	91	131	117	101	22	21.5
90	181	160	185		210	184	21	11.1
105	238			175	218	210	32	15.3
120	334		334	300	467	359	74	20.6
135	987	513	556		675	683	214	31.4
145				800	1050	925	177	19.1
160			1610			1610		
170		1120				1120		
Average variation coefficient								19.8

Table 15: Summary of viscosities of resins t06-t07

Resins t06 - t07					
Time	Viscosity 06	Viscosity t07	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	95	85	90	7	7.9
90	244	171	207.5	52	24.9
105	108	252	180	102	56.6
120	449	369	409	57	13.8
135	864	642	753	157	20.8
145		565	565		
150	1300		1300		
155		933	933		
Average variation coefficient					24.8

Table 16: Summary of viscosities of resins t08-t09

Resins t08 -t09					
Time	Viscosity t08	Viscosity t09	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	38	35	37	2	5.8
90	51	49	50	1	2.8
120	64	66	65	1	2.2
150	121	108	115	9	8.0
180	185	172	179	9	5.1
210	300	400	350	71	20.2
225	540	527	534	9	1.7
240	702	850	776	105	13.5
255	886	878	882	6	0.6
270	1000	1080	1040	57	5.4
Average variation coefficient					6.5

Table 17: Summary of viscosities of resins t10-t14

Resins t10 - t14								
Time	Viscosity t10	Viscosity t11	Viscosity t12	Viscosity t13	Viscosity t14	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	64	47	70	60	64	61	9	14.1
90	91	89	117	89	104	98	12	12.6
120	195	193	186	155	188	183	16	8.9
150	372	378	352	326	372	360	21	5.9
170	662	673	760	608	699	680	55	8.2
180	775	955	1010	650	650	808	168	20.8
185	859	1320	1330	802		1078	286	26.6
200	1080					1080		
205	1140					1140		
210					725	725		
235					840	840		
240					840	840		
255					1270	1270		
Average variation coefficient								13.9

Table 18: Summary of viscosities of resins t15-t16

Resins t15 - t16					
Time	Viscosity t15	Viscosity t16	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	70	80	75	7	9.4
90	140	126	133	10	7.4
120	202	205	204	2	1.0
150	353	411	382	41	10.7
165	650	495	573	110	19.1
180	629	567	598	44	7.3
195	628	714	671	61	9.1
210	996	834	915	115	12.5
220	1420	941	1181	339	28.7
Average variation coefficient					11.7

Table 19: Summary of viscosities of resins t17-t19

Resins t17 - t19						
Time	Viscosity t17	Viscosity t18	Viscosity t19	Mean	Standard Deviation	Variation Coefficient
[min]	[mPas]	[mPas]	[mPas]	[mPas]	[mPas]	[%]
60	63	65	64	64	1	1.6
90	105	98	102	102	4	3.5
120	198	167	195	187	17	9.2
150	407	382	363	384	22	5.7
165	538	498	494	510	24	4.8
180	667	588	618	624	40	6.4
195	765	713	735	738	26	3.5
210	822	899	902	874	45	5.2
220	837	1040	1090	989	134	13.5
245	1150	1040	1060	1083	59	5.4
Average variation coefficient						5.9

8.2 Results of Lap Shear Test

8.2.1 Treatment A1+

Treatment A1+ is defined in chapter 2.9.5 *Storage Conditions for the Specimens*

Table 20: Results of lap shear test based on ÖNORM EN 302-1 for treatment A1+

Treatment A1+									
Group	Sample Number	Fmax	Wood Failure		Fracture	Shear Strength			
			Single Value	Mean		Single Value	Mean	Std. Deviation	Variation Coefficient
[1]	[1]	[N]	[%]	[%]	[1]	[N/mm ²]	[N/mm ²]	[N/mm ²]	[1]
PF	0.21	2640	70	90	Valid	12.9	10.8	1.1	11%
PF	0.22	1900	100		Valid	9.3			
PF	0.23	2080	70		Valid	10.2			
PF	0.24	1890	100		Valid	9.2			
PF	0.25	2000	100		Valid	9.7			
PF	0.26	2190	90		Valid	10.8			
PF	0.34	2260	100		Valid	11.3			
PF	0.35	2220	100		Valid	11.0			
PF	0.36	2020	80		Valid	10.2			
PF	0.37	2210	100		Valid	11.0			
PF	0.38	2450	60		Valid	12.3			
PF	0.39	2340	90		Valid	11.7			
LPF 5%	5.21	2020	100	100	Valid	9.9	10.3	0.9	9%
LPF 5%	5.22	2140	100		Valid	10.6			
LPF 5%	5.23	1950	100		Valid	9.7			
LPF 5%	5.24	1760	100		Valid	8.6			
LPF 5%	5.25	2250	100		Valid	11.1			
LPF 5%	5.26	2090	100		Valid	10.2			
LPF 5%	5.34	2080	100		Valid	10.3			
LPF 5%	5.35	2290	100		Valid	11.3			
LPF 5%	5.36	2050	40		Valid	10.1			
LPF 5%	5.37	2350	100		Valid	11.6			
LPF 5%	5.38	2140	100		Valid	10.6			
LPF 5%	5.39	1820	100		Valid	9.0			
LPF 10%	10.21	1500	100	100	Valid	7.5	8.6	0.7	8%
LPF 10%	10.22	1630	100		Valid	8.0			
LPF 10%	10.23	1530	100		Valid	7.6			
LPF 10%	10.24	1670	100		Valid	8.3			
LPF 10%	10.25	1900	90		Valid	9.3			
LPF 10%	10.26	1760	100		Valid	8.7			
LPF 10%	10.34	1900	100		Valid	9.3			
LPF 10%	10.35	1810	100		Valid	8.9			
LPF 10%	10.36	1790	100		Valid	8.8			
LPF 10%	10.37	1910	100		Valid	9.3			

LPF 10%	10.38	1840	100		Valid	9.0			
LPF 10%	10.39	1680	100		Valid	8.2			
LPF 20%	20.21	1580	100	100	Valid	7.9	8.9	1.2	13%
LPF 20%	20.22	1510	100		Valid	7.6			
LPF 20%	20.23	1450	100		Valid	7.2			
LPF 20%	20.24	1540	100		Valid	7.7			
LPF 20%	20.25	1470	100		Valid	7.3			
LPF 20%	20.34	1890	100		Valid	9.3			
LPF 20%	20.35	1880	100		Valid	9.3			
LPF 20%	20.36	1730	100		Valid	8.6			
LPF 20%	20.37	1800	100		Valid	8.9			
LPF 20%	20.38	1910	100		Valid	9.3			
LPF 20%	20.39	2130	100		Valid	10.5			
LPF 20%	20.4	2060	100		Valid	10.2			
LPF 20%	20.41	2010	100		Valid	10.0			
LPF 20%	20.42	2110	100		Valid	10.5			
LPF 20%	20.43	2050	100		Valid	10.0			
LPF 30%	30.21	1330	100	100	Valid	6.7	8.1	0.9	11%
LPF 30%	30.22	1390	100		Valid	7.0			
LPF 30%	30.27	1350	70		Valid	6.8			
LPF 30%	30.33	1750	100		Valid	8.7			
LPF 30%	30.34	1770	100		Valid	8.8			
LPF 30%	30.35	1890	100		Valid	9.4			
LPF 30%	30.36	1760	100		Valid	8.8			
LPF 30%	30.37	1770	100		Valid	8.8			
LPF 30%	30.38	1730	100		Valid	8.6			
LPF 30%	30.39	1870	100		Valid	9.3			
LPF 30%	30.4	1690	100		Valid	8.4			
LPF 30%	30.41	1440	100		Valid	7.1			
LPF 30%	30.42	1830	100		Valid	9.0			
LPF 30%	30.43	1510	100		Valid	7.5			
LPF 30%	30.44	1450	100		Valid	7.2			
LPF 30%	30.45	1680	100		Valid	8.4			
LPF 40%	40.21	1790	100	100	Valid	9.0	8.7	0.9	10%
LPF 40%	40.22	1920	100		Valid	9.5			
LPF 40%	40.23	1590	100		Valid	7.9			
LPF 40%	40.24	1800	100		Valid	8.9			
LPF 40%	40.25	1920	100		Valid	9.6			
LPF 40%	40.26	1830	100		Valid	9.2			
LPF 40%	40.34	1640	100		Valid	8.2			
LPF 40%	40.35	1870	100		Valid	9.3			
LPF 40%	40.36	1580	100		Valid	7.9			
LPF 40%	40.37	1910	100		Valid	9.6			
LPF 40%	40.38	1560	100		Valid	7.9			
LPF 40%	40.39	1380	90		Valid	6.9			

8.2.2 Treatment A2

Treatment A2 is defined in chapter 2.9.5 *Storage Conditions of the Specimens*

Table 21: Results of lap shear test based on ÖNORM EN 302-1 for treatment A2

Treatment A2									
Group	Sample Number	Fmax	Wood Failure		Fracture	Shear Strength			
			Single Value	Mean		Single Value	Mean	Std. Deviation	Variation Coefficient
[1]	[1]	[N]	[%]	[%]	[1]	[N/mm ²]	[N/mm ²]	[N/mm ²]	[1]
PF	0.03	870	100	70	Valid	4.1	4.5	0.8	18%
PF	0.04	902	100		Valid	4.2			
PF	0.08	774	100		Valid	3.7			
PF	0.09	698	100		Valid	3.3			
PF	0.1	1070	100		Valid	5.1			
PF	0.11	1080	100		Valid	5.1			
PF	0.12	1100	100		Valid	5.3			
PF	0.14	1130	100		Valid	5.4			
PF	0.16	783	0		Valid	3.6			
PF	0.17	968	0		Valid	4.5			
PF	0.18	940	0		Valid	4.4			
PF	0.2	1280	0		Valid	6.0			
LPF 5%	5.05	895	0	20	Valid	4.2	3.2	1.2	38%
LPF 5%	5.07	441	0		Valid	2.1			
LPF 5%	5.08	946	0		Valid	4.4			
LPF 5%	5.09	1250	100		Valid	5.8			
LPF 5%	5.1	708	0		Valid	3.4			
LPF 5%	5.11	605	0		Valid	2.9			
LPF 5%	5.12	807	100		Valid	3.8			
LPF 5%	5.13	356	0		Valid	1.7			
LPF 5%	5.14	638	0		Valid	3.0			
LPF 5%	5.15	507	0		Valid	2.4			
LPF 5%	5.16	655	0		Valid	3.0			
LPF 5%	5.17	370	0		Valid	1.7			
LPF 10%	10.01	921	20	30	Valid	4.1	3.9	0.8	20%
LPF 10%	10.02	802	10		Valid	3.9			
LPF 10%	10.03	693	10		Valid	3.3			
LPF 10%	10.04	1070	30		Valid	5.2			
LPF 10%	10.05	722	20		Valid	3.5			
LPF 10%	10.06	623	20		Valid	3.0			
LPF 10%	10.08	1020	40		Valid	4.9			
LPF 10%	10.1	1080	50		Valid	5.2			
LPF 10%	10.11	614	0		Valid	2.9			

LPF 10%	10.16	784	50		Valid	3.7			
LPF 10%	10.17	767	40		Valid	3.7			
LPF 10%	10.18	705	50		Valid	3.4			
LPF 20%	20.01	1080	100	100	Valid	5.1	5.0	0.3	5%
LPF 20%	20.02	975	100		Valid	4.6			
LPF 20%	20.03	1130	100		Valid	5.3			
LPF 20%	20.04	1030	90		Valid	4.8			
LPF 20%	20.05	1040	100		Valid	4.9			
LPF 20%	20.06	1030	100		Valid	4.9			
LPF 20%	20.07	1130	80		Valid	5.3			
LPF 20%	20.08	1030	100		Valid	4.9			
LPF 20%	20.15	1120	100		Valid	5.3			
LPF 20%	20.17	1130	100		Valid	5.4			
LPF 20%	20.19	1000	100		Valid	4.8			
LPF 20%	20.2	997	100		Valid	4.8			
LPF 30%	30.01	843	0	10	Valid	4.0	4.2	0.5	13%
LPF 30%	30.07	1060	0		Valid	4.9			
LPF 30%	30.08	1110	0		Valid	5.2			
LPF 30%	30.09	922	30		Valid	4.3			
LPF 30%	30.13	812	0		Valid	3.8			
LPF 30%	30.14	1000	0		Valid	4.7			
LPF 30%	30.15	815	10		Valid	3.8			
LPF 30%	30.16	794	20		Valid	3.7			
LPF 30%	30.17	796	0		Valid	3.7			
LPF 30%	30.18	952	20		Valid	4.1			
LPF 30%	30.19	1040	80		Valid	4.8			
LPF 30%	30.2	780	0		Valid	3.7			
LPF 40%	40.05	1090	80	40	Valid	5.2	4.7	1.5	31%
LPF 40%	40.06	1220	80		Valid	5.8			
LPF 40%	40.07	1030	80		Valid	4.9			
LPF 40%	40.1	1310	80		Valid	6.2			
LPF 40%	40.11	272	10		Valid	1.3			
LPF 40%	40.12	855	20		Valid	3.7			
LPF 40%	40.13	1370	60		Valid	6.4			
LPF 40%	40.14	921	0		Valid	4.3			
LPF 40%	40.15	1360	20		Valid	6.4			
LPF 40%	40.16	813	30		Valid	3.6			
LPF 40%	40.17	897	20		Valid	4.3			
LPF 40%	40.18	960	20		Valid	4.6			

8.3 Results of the Statistical Evaluation

All the results are obtained from the software SPSS

8.3.1 Treatment A1+

Table 22: Test of normality of the groups for treatment A1+

		Kolmogorov-Smirnov ^a			Shapiro-Wilk		
		Statistik	df	Signifikanz	Statistik	df	Signifikanz
Shear Strength [N/mm ²]	PF	.123	12	.200 [*]	.966	12	.862
	LPF 5%	.110	12	.200 [*]	.971	12	.922
	LPF 10%	.150	12	.200 [*]	.920	12	.286
	LPF 20%	.150	15	.200 [*]	.907	15	.123
	LPF 30%	.219	16	.038	.879	16	.038
	LPF 40%	.207	12	.163	.888	12	.110

a. Signifikanzkorrektur nach Lilliefors

*. Dies ist eine untere Grenze der echten Signifikanz.

Table 23: Test for homogenous variances of the groups at treatment A1+

Shear Strength [N/mm ²]			
Levene-Statistik	df1	df2	Signifikanz
1.513	5	73	.196

Table 24: Oneway ANOVA for treatment A1+

Shear Strength [N/mm ²]					
	Quadratsumme	df	Mittel der Quadrate	F	Signifikanz
Zwischen den Gruppen	70.768	5	14.154	15.152	.000
Innerhalb der Gruppen	68.190	73	.934		
Gesamt	138.959	78			

Table 25: Results of the Post Hoc Test

Scheffé-Prozedur^{a,b}

Shear Strength [N/mm ²]	N	Untergruppe für Alpha = 0.05.	
		1	2
PF	12		10.7967
LPF 5%	12		10.2500
LPF 10%	12	8.5800	
LPF 20%	15	8.9467	
LPF 30%	16	8.1375	
LPF 40%	12	8.6667	
Signifikanz		.480	.837

Die Mittelwerte für die in homogenen Untergruppen befindlichen Gruppen werden angezeigt.

a. Verwendet ein harmonisches Mittel für Stichprobengröße = 12.973.

b. Die Gruppengrößen sind nicht identisch. Es wird das harmonische Mittel der Gruppengrößen verwendet.

Fehlerniveaus des Typs I sind nicht garantiert.

8.3.2 Treatment A2

Table 26: Test of normality of the groups for treatment A2

		Kolmogorov-Smirnov ^a			Shapiro-Wilk		
		Statistik	df	Signifikanz	Statistik	df	Signifikanz
Shear Strength [N/mm ²]	PF	.146	12	.200 [*]	.968	12	.892
	LPF 5%	.138	12	.200 [*]	.948	12	.615
	LPF 10%	.182	12	.200 [*]	.893	12	.129
	LPF 20%	.245	12	.045	.900	12	.158
	LPF 30%	.192	12	.200 [*]	.870	12	.066
	LPF 40%	.142	12	.200 [*]	.915	12	.247

a. Signifikanzkorrektur nach Lilliefors

*. Dies ist eine untere Grenze der echten Signifikanz.

Table 27: Test for homogenous variances of the groups at treatment A2

Shear Strength [N/mm ²]			
Levene-Statistik	df1	df2	Signifikanz
3.932	5	66	.004

Table 28: Oneway ANOVA for treatment A2

Shear Strength [N/mm ²]					
	Quadratsumme	df	Mittel der Quadrate	F	Signifikanz
Zwischen den Gruppen	24.931	5	4.986	5.594	.000
Innerhalb der Gruppen	58.826	66	.891		
Gesamt	83.757	71			

Table 29: Comparison of the groups with each other after Tamhan for treatment A2

Shear Strength [N/mm²]

Tamhane

(I) Group	(J) Group	Mittlere Differenz (I-J)	Standardfehler	Signifikanz	95%-Konfidenzintervall	
					Untergrenze	Obergrenze
—	LPF 5%	1.3366667	.4264220	.078	-.085564	2.758898
	LPF 10%	.6533333	.3308962	.611	-.432543	1.739210
	LPF 20%	-.4541667	.2506908	.768	-1.347337	.439003
	LPF 30%	.3116667	.2841083	.994	-.640123	1.263457
	LPF 40%	-.1708333	.4894786	1.000	-1.830382	1.488715
—	PF	-1.3366667	.4264220	.078	-2.758898	.085564
	LPF 10%	-.6833333	.4206121	.855	-2.091224	.724557
	LPF 20%	-1.7908333 ⁺	.3609267	.005	-3.103290	-.478377
	LPF 30%	-1.0250000	.3848893	.235	-2.361238	.311238
	LPF 40%	-1.5075000	.5540862	.175	-3.333046	.318046
—	PF	-.6533333	.3308962	.611	-1.739210	.432543
	LPF 5%	.6833333	.4206121	.855	-.724557	2.091224
	LPF 20%	-1.1075000 ⁺	.2406755	.007	-1.962316	-.252684
	LPF 30%	-.3416667	.2753113	.980	-1.260638	.577304
	LPF 40%	-.8241667	.4844256	.818	-2.473486	.825152

PF	.4541667	.2506908	.768	-.439003	1.347337
LPF 5%	1.7908333*	.3609267	.005	.478377	3.103290
LPF 10%	1.1075000*	.2406755	.007	.252684	1.962316
– LPF 30%	.7658333*	.1707335	.006	.179637	1.352030
LPF 40%	.2833333	.4336147	1.000	-1.303414	1.870081
PF	-.3116667	.2841083	.994	-1.263457	.640123
LPF 5%	1.0250000	.3848893	.235	-.311238	2.361238
LPF 10%	.3416667	.2753113	.980	-.577304	1.260638
– LPF 20%	-.7658333*	.1707335	.006	-1.352030	-.179637
LPF 40%	-.4825000	.4537547	.996	-2.083419	1.118419
PF	.1708333	.4894786	1.000	-1.488715	1.830382
LPF 5%	1.5075000	.5540862	.175	-.318046	3.333046
LPF 10%	.8241667	.4844256	.818	-.825152	2.473486
– LPF 20%	-.2833333	.4336147	1.000	-1.870081	1.303414
LPF 30%	.4825000	.4537547	.996	-1.118419	2.083419

*. Die Differenz der Mittelwerte ist auf dem Niveau 0.05 signifikant.